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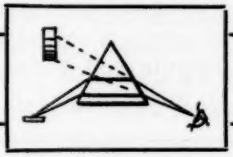

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THE INTERRELATION OF VARIOUS ASPECTS OF COLOR VISION*

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I. The Data of Color Vision

Quantitative measurements of normal color vision have been concerned with four aspects of the process: color mixture, spectrum luminosity, hue discrimination, and saturation. It is my purpose to show that these different measurements are quantitatively related to one another. In order to do this profitably it is necessary first to describe briefly the origins and nature of the data.

The measurements of color mixture record the relative proportions in which three spectral primaries need to be superimposed on the retina in order to duplicate the sensations produced by different monochromatic portions of the spectrum. Though the earliest, reasonably adequate measurements of this kind were made by Maxwell (21), the first complete measurements were not made until somewhat later by Koenig and Dieterici (19). Their data plus the data of Abney (1) were recomputed and averaged several years ago by Weaver (27) and have since become the familiar excitation curves recommended and used as standard by the Optical Society of America. These curves will be found in Fig. 8, shown later in this paper. Recently the measurements have been

* Presented at the New York meeting of the Optical Society of America on February 28, 1931.

made anew by Wright (29), who has worked over the whole matter from a fresh viewpoint and with a new technic. Fortunately, as Wright has shown, his measurements, though differing in detail from those of Koenig and Dieterici and of Abney, are essentially identical with them. The general form of the color mixture relationship is therefore well established at the present time, though many measurements will still be required to describe the condition in the average eye.

Efforts to describe the relative brightness of different portions of the spectrum are over a century old, and have been made frequently since. The best of the earlier measurements were made by Koenig (17) about forty years ago, and are still quite good. The more modern of such measurements are by Ives (11), by Nutting (22), by Hyde, Forsythe and

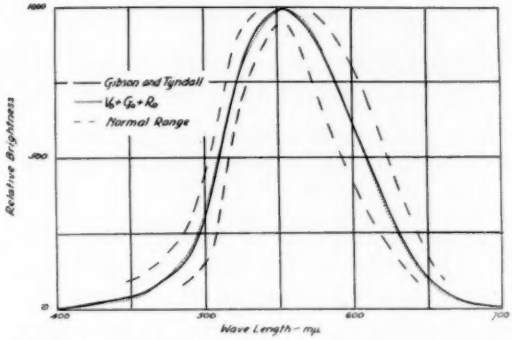

FIG. 1. *Visibility of the spectrum. The continuous line represents the average data of Gibson and Tyndall computed so as to refer to Abbot-Priest sunlight. The light, dashed lines indicate the range within which fall the measurements of the completely studied, normal observers in this investigation. The dotted line represents the sum of the cone primaries* V_0, G_0, *and* R_0.

Cady (10), and by Coblentz and Emerson (2), all of whom employed many observers; other investigations involving few observers could be cited (28) if one were interested in a complete historical statement. Probably the most adequate set of data on the visibility of the spectrum are those secured by Gibson and Tyndall (4) with fifty-two subjects. Fig. 1 shows the results of this investigation. The figure gives not merely the average, but the range of variation encountered in dealing with different observers possessing normal color vision.

The third aspect of color vision, namely hue discrimination in the spectrum, is not nearly so well documented as the relative luminosity of the spectrum. The measurements consist in determining the minimum difference apart in wave length, $\Delta\lambda$, which lights of two wave lengths

must be in order that they may be recognized as differing in hue. Many scattered observations are in existence (28); but the only complete measurements of this visual function are by Steindler (26), by Jones (13) and by Laurens and Hamilton (20). These measurements, as well as the less complete ones of other workers, have shown that there are four maxima of hue discrimination: two major ones, at about 490 $m\mu$ and 575 $m\mu$ respectively, and two minor ones at about 430 $m\mu$ and 625 $m\mu$ respectively. Fig. 7, found later in this paper, shows that even under identical conditions the precise relationship varies surprisingly from person to person; the general form, however, is reasonably constant.

Quantitative expressions for the saturation of spectrum colors are derived more indirectly from actual measurements than is the case with the other properties of color vision already mentioned. It is a familiar subjective judgment that homogenous spectral lights are not equally saturated and that some of them produce more white sensation than others. It was Helmholtz (7) who first pointed out the relation of these judgments to measurements of the relative brightness of complementary colors. He supposed that the reason that homogenous yellow and homogenous violet require such widely different brightnesses to make white is that yellow is much less saturated than violet. In terms of this idea the relative luminosities of spectral complementaries are an inverse measure of their saturation. The most complete data of this kind are by Sinden (25). They are given in Table 1. Sinden actually gives the ratios L_1/L_2 of the luminosities for each pair of complementaries; but knowing from his specifications that their sum equals 75 photons, it has

TABLE 1. *Relative luminosities of spectral complementaries. Data from Sinden (25).*

Complementaries		Luminosities	
λ_1	λ_2	L_1	L_2
650	496	31.6	43.4
609	493.5	39.3	35.7
591	490	50.3	24.7
586	487.5	55.4	19.6
580	482.5	62.0	13.0
578.5	480.5	64.2	10.8
576.5	477.5	65.8	9.2
575.5	474.5	67.7	7.3
574	472	69.0	6.0
573	466.5	70.6	4.4
572	459	72.1	2.9
570.5	443	73.2	1.8

been simple to compute the separate brightness of each member of the pair. Less complete data by other people show essentially the same relationship.

A totally different approach to saturation has been made by Priest and Brickwedde (24). These investigators measured the minimum brightness of homogeneous spectral light which has to be added to one half of a neutral (white) photometric field of constant brightness in order to produce a perceptible color difference between the two halves of the field. The ratio of the added brightness of the spectral color to the total brightness they call the least perceptible colorimetric purity. It is clear that such data give us information about the relative saturation of spectral colors, since the more white sensation a colored light carries with it, the more of that light will be required to be added to white in order to produce a minimal color sensation. The data secured by Priest and Brickwedde (24) are given in Fig. 4 reproduced later in this paper. To my knowledge they are the only data of this kind in existence, and I am indebted to Dr. Priest for his kindness in permitting me to use them before their final publication.

It has been a commonly accepted notion that these various aspects of color vision are merely different manifestations of a basic, physiological mechanism concerned with color reception. The ideal has therefore been to build a hypothetical structure—a theory of color vision—which would show these interrelations, and which, when specified precisely, would yield *quantitatively* the various data presented above. Unfortunately this has been only an ideal, not even remotely realized. Occasionally two sets of data have been correlated; rarely three. This has not been for want of ideas. The ideas for such a theoretical formulation have surely been long available. Beginning with Young (30) and continuing with Helmholtz (7), Hering (9), Fick (3), Koenig (19) and others (28), there has been a steady outpouring of relevant and important ideas on the subject. What has been lacking has been a certain objectively critical perseverance which would sort out these ideas and would follow through their quantitative implications; which would combine some, eliminate others, and reach some kind of unity of thought about them.

At the Thomas Young Memorial Meeting in 1929 at Cornell University I presented to the Optical Society a preliminary effort (5) at such a reformulation of ideas. The discussion then and since has shown that such an attempt, though tentative and incomplete, was not inopportune and that further work might prove both fruitful and stimulating. The

result of this new work constitutes the present contribution. The ideas involved are the same and are just as tentative as before. But their further development is presented here as a record of progress, coupled with the hope that others might be induced to modify, extend, and test them so that they may become reasonably well defined and established.

II. A TENTATIVE, HYPOTHETICAL COLOR SYSTEM

The various measurements just enumerated have been secured by different investigators, under different conditions and with different numbers of individuals. Some represent the averages of many individuals, some the average of readings with a single individual, and some are single readings. Thus these measurements, though fully adequate to describe the essential, quantitative elements of the various aspects of color vision, do not constitute a homogenous body of data descriptive of color vision. Therefore, at the outset it is well to recognize that it is not possible to construct a single theoretical color system in terms of which *all* these measurements may be derived precisely and quantitatively.

Instead, there are two procedures that can be followed. A color system may be proposed which will yield an approximately quantitative agreement with all the data; the deviations from theory may then be discussed whenever possible in the light of known individual variation. Or a color system may be proposed which will yield a perfect agreement with some data and an approximate agreement with others. Since all the properties of color vision are assumed to be functionally related aspects of one receptor mechanism, it is entirely arbitrary which aspects are chosen for approximate and which for precise derivation. For reasons which will become apparent, I have chosen the second alternative as a means of presenting the ideas here involved.

The curves V, G, R suggested at the Thomas Young Memorial Meeting (5), and reproduced in Fig. 2, constitute such a description of the color receptor system. The curves were designed to describe perfectly three of the five sets of data enumerated above, and to give approximately the two others. The curves V, G, R, may be considered purely as mathematical functions from which, in terms of certain rules of computation, other functions resembling the data may be derived. But it is better to think of them more realistically, even though only approximately, as the sensibility distributions of three species of cones.

It is supposed, as a modern statement of Young's original idea, that there are these three kinds of cones present in the retina, and that in the fovea they exist in approximately equal numbers. The sensations which

result from the action of these three cones are qualitatively specific and may be tentatively described as blue, green and red respectively. Thus a given cone, which contains a photosensitive substance whose spectral absorption is greater in the blue, or in the green, or in the red, is joined to a nerve fiber which is so connected with the brain that when the photosensitive substance in the cone is changed by light and starts an impulse in the nerve, the nerve will register respectively blue or green or red in the brain. It should be emphasized that regardless of the method used for starting this impulse, and regardless of the wave length of the stimulating light, and indeed regardless of the nature of the photosensitive substance, an impulse proceeding along a "blue" nerve will register blue in the brain, a "green" nerve green and a "red" nerve red. I have

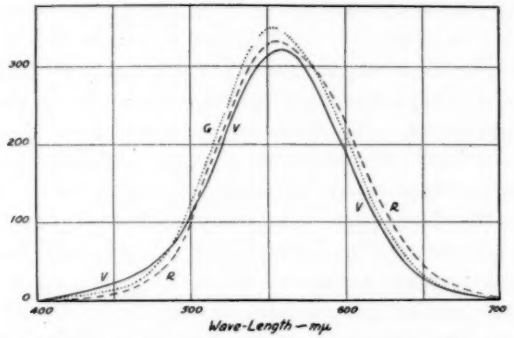

FIG. 2. *A tentative set of cone primaries, designed to describe perfectly the data of colorimetric purity, of visibility and of hue discrimination,—and to describe approximately the data of complementary color luminosity and of color mixture.*

already discussed (5) the reasons for speaking of a "blue" cone instead of a "violet" cone (even though its corresponding sensibility curve is labelled *V*) and shall not enter into that matter here again.

It is necessary to describe exactly what these curves represent. The abscissas are wave lengths. The ordinates are the reciprocals of the energies required at the different wave lengths to produce the same intensity of sensation in a given species of cone. This means that if we could investigate separately the activity, say of the red cones alone, and were to measure the energy required to produce the same red sensation qualitatively and quantitatively with different wave lengths in the spectrum, then the reciprocals of these energies would yield a curve such as the *R* curve in Fig. 2. The same holds for the other two curves. The ordinates in Fig. 2 are therefore brightness values. If what has been

found for visual purple (6) holds for the sensitive substances in the cones, then the curves in Fig. 2 are very nearly the absorption spectra of the three sensitive materials.

The novel thing about the curves V, G, R is the fact that they resemble one another more than they differ from one another. The hypothetical curves drawn for the trireceptor theory by various people beginning with Helmholtz have in each case differed widely from one another in shape and in spectral distribution. The V, G, R curves not only resemble one another, but resemble as well the spectrum visibility curve at high illuminations.

Each curve represents the respective brightness function of the corresponding cones in the fovea. The sum of the curves therefore gives the brightness distribution of the spectrum for white light. The particular cone primaries V, G, R, were constructed to yield, in this way, a point-for-point agreement with the spectrum visibility data of Ives (12), and naturally they do so (5). As stated above the three species of cones are assumed to be present in the fovea in approximately equal numbers. Corresponding to this, the areas included under the curves V, G, and R, are to each other as 0.97:1.03:1.02.

These cone primaries were built to yield perfectly not only the visibility function of Ives, but the colorimetric purity data of Priest and Brickwedde as well. Least perceptible colorimetric purity is assumed to be inversely proportional to the saturation of the spectrum as deduced from the V G R cone primaries. Saturation here is defined as the ratio of the "color" luminosity to the total luminosity at any wave length. The total luminosity is simply the sum $V+G+R$. Since when $V=G=R$ the resulting sensation is white, then "color" luminosity is the total luminosity minus three times the luminosity of the lowest cone primary. Thus up to about 500 $m\mu$ the "color" luminosity is $V+G+R-3R$, whereas beyond 500 $m\mu$ it is $V+G+R-3V$. As already shown (5) the cone primaries V, G, R, when computed in this way reproduce precisely the average data of Priest and Brickwedde.

The third set of data which the curves V, G, and R were designed to duplicate perfectly is the measurement of hue discrimination for Laurens' own eye. Following the general idea first suggested by Helmholtz (8), hue changes in the spectrum are considered as depending on the way in which the cone primaries in Fig. 2 change in relation to each other. As a first approximation and for the sake of simplicity in computation it is supposed that the hue change $dH/d\lambda$ depends on the difference between the rates of change of the two most rapidly changing cone prim-

aries. Thus up to about 500 $m\mu$ $dH/d\lambda$ is proportional to $d(V-G)/d\lambda$ whereas beyond that to $d(R-G)/d\lambda$. The actual data record $\Delta\lambda$ measurements and are therefore inversely proportional to these functions. When worked over in detail, computation and measurement agree precisely (5), since the curves V, G, and R were in reality derived by the reverse procedure from the hue discrimination data.

The data of visibility, of colorimetric purity, and of hue discrimination have thus entered into the construction of the curves V, G, and R, and have defined them as a color system capable of describing these aspects of color vision with perfect precision. What relation does this color system bear to the other two groups of data? Computation shows that one set of measurements, namely, the relative luminosities of spectral complementaries correspond with an excellent degree of approximation to theoretical expectation from the cone primaries V, G, R. For example it was found (5) from Sinden's data that when the values V_1, G_1, and R_1 corresponding to the luminosity L_1 of one of a pair of complementaries are added to the cone values V_2, G_2, and R_2 corresponding to the luminosity L_2 of the other member of the pair, the sum is such that $V_1+V_2=G_1+G_2=R_1+R_2$ to within a very small percentage error.

Finally, the data of color mixture come out from the color system V, G, R, in an obviously approximate, but distinctly encouraging manner. For example from the standard excitation curves already mentioned it has been possible (5) by homogeneous, linear transformations to construct three curves which resemble the curves V, G, R within a few percent.

III. Color Systems Assuming Color Mixture Data

In order to show that the ideas which underlie these derivations of color vision are unaffected by this particular choice of functions for exact and approximate derivation, it becomes necessary to present the results of other choices involving different values for the spectral distributions of the three cone primaries. Because V, G, and R give a color mixture function which is only approximately correct, I shall deal first with systems that will yield color mixture equations which are perfectly correct.[1]

Consider the color system whose cone primaries are V_0, G_0, and R_0

[1] This development of the ideas suggested in my Thomas Young address has become doubly necessary because of a recent paper by Judd (16) in which he has taken elaborate exception to the adequacy with which the particular cone primaries V, G, and R reproduce the standard data of color mixture. It is apparent that so far as concerns the adequacy of the ideas under consideration, the present treatment renders Judd's paper without point.

given in Fig. 3. These primaries have been made up, point for point, directly from the standard excitation curves, v_0, g_0, and r_0 for white light, by the equations

$$V_0 = .033v_0 + .557g_0 + .396r_0 \quad [1]$$

$$G_0 = .008v_0 + .607g_0 + .399r_0 \quad [2]$$

$$R_0 = .003v_0 + .477g_0 + .519r_0 \quad [3]$$

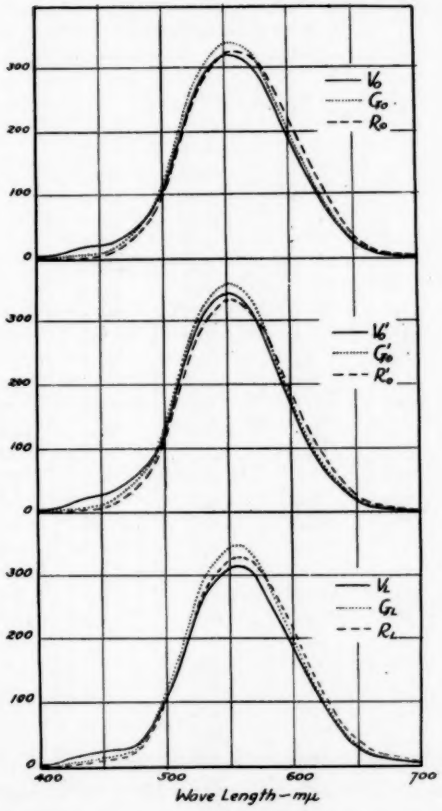

FIG. 3. *Several sets of cone primaries designed for different purposes. The set $V_0G_0R_0$ describes visibility and color mixture perfectly, and hue discrimination and saturation approximately. The set $V_0'G_0'R_0'$ is a slight variant of $V_0G_0R_0$ and deals especially with colorimetric purity. The set $V_LG_LR_L$ is especially concerned with hue discrimination.*

which involve the following steps in computation. The excitation curves v, g, and r describe the standard data of color mixture referred to an

equal energy spectrum. Since the functions V_0, G_0, and R_0 refer to white light, the values v, g, and r must also be transformed to refer to white light. These transformed values are v_0, g_0, and r_0. The values for v, g, and r are the standard values and are given in Table 2. They are multiplied by the energy distribution (E) of Abbot-Priest sunlight (23)(15) the values for which are given in Table 2. Then in order to make the

TABLE 2. *Excitation curves derived from the computations of Weaver* (27) *based on the data of Koenig and Dieterici* (19) *and Abney* (1). *Energy distribution in Abbot-Priest sunlight* (23) (15).

λ in mμ	v	g	r	E	v_0	g_0	r_0
400	253			.614	95.0		
410	433			.666	176.4		
420	614	1		.715	268.5	.5	
430	915	3		.761	426.0	1.4	
440	1019	7		.805	501.7	3.5	
450	950	16		.844	490.4	8.4	
460	842	38	1	.880	453.0	20.8	.5
470	697	81	4	.910	388.0	45.9	2.2
480	473	122	14	.939	271.5	71.3	8.1
490	220	169	41	.962	129.5	101.3	24.2
500	123	260	83	.982	73.8	158.9	50.0
510	87	391	151	.997	53.0	242.8	92.4
520	61	510	233	1.009	37.6	320.2	144.2
530	43	572	307	1.017	26.7	362.1	191.5
540	29	603	373	1.020	18.1	383.1	233.6
550	18	612	424	1.022	11.3	389.2	265.8
560	11	578	466	1.018	6.9	366.2	291.0
570	7	517	505	1.014	4.3	326.4	314.2
580	4	415	520	1.009	2.5	260.7	322.0
590	2	296	535	1.000	1.2	184.2	328.2
600	1	196	510	.987	.6	120.5	309.1
610		113	462	.974		68.5	276.2
620		59	375	.956		35.1	219.9
630		29	285	.937		16.9	164.0
640		10	195	.923		5.7	110.5
650		3	118	.903		1.7	65.4
660		1	68	.886		.6	37.0
670			40	.862			21.2
680			22	.843			11.4
690			13	.819			6.5
700			8	.795			3.7

areas under v_0, g_0, and r_0 equal to one another and also equal to the areas under V_0, G_0, and R_0, we write $v_0 = 0.6112vE$; $g_0 = 0.6223gE$; and $r_0 = 0.6135rE$. The values of v_0, g_0, and r_0 so secured are also given in

Table 2, and may now be introduced into equations [1] [2] and [3]. The resulting values of V_0, G_0, and R_0 are given in Table 3. Thus, by construction, V_0, G_0, and R_0 give an exact description of color mixture data.

TABLE 3. *Values of three sets of hypothetical cone primaries.*

λ in $m\mu$	V_0	G_0	R_0	V_0'	G_0'	R_0'	V_L	G_L	R_L
400	3.1	.8	.3	4.0	1.0	.4	5.4	1.1	1.0
410	5.8	1.4	.5	7.4	1.8	.7	7.0	1.7	1.4
420	9.1	2.4	1.0	11.6	3.0	1.3	12.9	6.5	5.2
430	14.9	4.3	2.0	18.9	5.3	2.6	17.6	9.5	7.6
440	18.5	6.1	3.2	23.6	7.6	4.1	22.2	11.5	9.3
450	20.9	9.0	5.5	26.6	11.1	7.0	25.6	14.5	11.7
460	26.7	16.5	11.6	34.1	20.0	14.6	27.2	18.0	14.5
470	39.3	31.9	24.2	49.9	38.4	30.1	31.2	24.6	20.0
480	51.9	48.7	39.0	64.8	57.6	47.2	45.3	43.2	35.8
490	70.3	72.2	61.3	84.3	82.7	70.6	70.8	76.8	65.4
500	110.8	117.0	102.0	129.7	131.8	114.7	108.4	120.9	105.2
510	173.6	184.7	163.9	199.4	205.2	180.8	158.0	175.7	158.6
520	236.7	252.2	227.7	267.1	276.5	246.5	219.8	244.5	223.9
530	278.4	296.4	272.2	308.2	320.4	289.1	268.2	298.3	275.0
540	306.5	325.9	304.0	333.0	347.4	317.1	293.5	326.1	302.8
550	322.5	342.4	323.7	344.9	360.7	332.6	311.9	345.4	324.9
560	319.5	338.5	325.8	334.2	350.7	327.8	313.7	346.3	329.8
570	306.4	323.5	318.8	310.9	327.7	312.2	299.2	328.3	319.1
580	272.8	286.7	291.5	265.3	281.3	275.2	261.3	283.2	287.0
590	232.6	242.8	258.2	211.6	226.5	231.2	224.3	239.8	253.8
600	189.5	196.5	217.9	161.1	174.2	185.7	186.2	196.6	216.3
610	147.5	151.8	176.0	115.7	126.8	142.3	140.3	147.7	164.1
620	106.6	109.1	130.9	78.1	86.6	101.5	104.2	109.2	123.1
630	74.4	75.7	93.2	51.6	57.7	70.1	73.6	76.8	87.8
640	47.0	47.6	60.1	30.7	34.7	43.8	46.9	48.5	56.8
650	26.8	27.1	34.7	16.9	19.3	24.9	33.7	34.7	41.3
660	14.9	15.1	19.4	9.3	10.6	13.8	19.6	19.7	25.0
670	8.4	8.5	11.0	5.1	5.8	7.7	15.4	15.4	19.7
680	4.5	4.5	5.9	2.7	3.1	4.2	12.0	12.0	15.3
690	2.6	2.6	3.4	1.6	1.8	2.4	8.8	8.8	11.3
700	1.5	1.5	1.9	.9	1.0	1.3	5.8	5.8	7.4

It is to be emphasized that there is an infinite number of primaries which can accomplish the same thing. Any coefficients placed in front of v_0, g_0, and r_0 in the above equations will yield a set of curves, which are linear and homogeneous transformations of v_0, g_0, and r_0, and will therefore give a perfect description of the color mixture data incorporated in them. However, V_0, G_0, and R_0 have the additional property of yielding a visibility curve which is in practically perfect agreement with the average, normal visibility curve.

The visibility of the spectrum of white light is given by the simple addition of the three cone primaries. Adding equations [1], [2], and [3] we get

$$V_0 + G_0 + R_0 = .044v_0 + 1.641g_0 + 1.314r_0 \qquad [4]$$

which is comparable with the luminosity curve. To show this, divide equation [4] by [3] so as to make the area of the luminosity curve the same as the area of v_0 or g_0 or r_0. This gives

$$L_0 = \frac{(V_0 + G_0 + R_0)}{3} = .015v_0 + .547g_0 + .438r_0 \qquad [5]$$

for the composition of the luminosity function L_0. These coefficients for v_0, g_0, and r_0 are identical with those used by Judd (14) to give the best description of the average visibility curve of Gibson and Tyndall. Fig. 1 shows a comparison of the values given by the sum $V_0+G_0+R_0$ with the experimental values of Gibson and Tyndall also made to refer to Abbot-Priest sunlight. As a matter of fact, the three sets of cone primaries shown in Fig. 3 and the set shown in Fig. 2 are so similar that their respective visibility curves are practically the same.

It will be recalled that the areas under V_0, G_0, and R_0 should be approximately equal to one another to express the fact that the three species of cone are present in about equal numbers in the fovea. As may by judged by equations [1], [2], and [3] these areas are 0.986 for V_0, 1.004 for G_0, and 0.999 for R_0.

Thus the color system represented by the cone primaries V_0, G_0, and R_0 gives color mixture and spectrum luminosity in exact agreement with the data. The remaining two properties—saturation and hue discrimination—are given only approximately. It is instructive to consider these carefully.

As previously explained, the saturation, S_λ, of a given color in the spectrum may be derived from one or the other of the two ratios $(V_0+G_0-2R_0)/(V_0+G_0+R_0)$ and $(G_0+R_0-2V_0)/(V_0+G_0+R_0)$ depending on whether λ lies on the blue side of 550 $m\mu$ or on the red side. This rests on the supposition that for a given wave length λ the total luminosity minus its "white" luminosity gives its "color" luminosity. Examination of the curves for V_0, G_0, and R_0 shows that to the blue side of 550 $m\mu$ the lowest cone primary is R_0, and to the red side it is V_0. Hence the "white" luminosity is equivalent to $3R_0$ and to $3V_0$ respectively, and the "color" luminosity to $V_0+G_0-2R_0$ and to $G_0+R_0-2V_0$ respectively. I shall leave for the future the nice point as to whether

this "color" luminosity itself is to be considered completely saturated, as I am assuming here, or as partly saturated because it is often made up of the luminosities of two cone primaries. For present purposes the assumption of complete saturation is the simpler. We may then write

$$S_{\lambda<550} = \frac{V_0 + G_0 - 2R_0}{V_0 + G_0 + R_0} \qquad [6]$$

$$S_{\lambda>550} = \frac{G_0 + R_0 - 2V_0}{V_0 + G_0 + R_0} \qquad [7]$$

to express the saturation relationships in the spectrum.

In Priest and Brickwedde's experiments let B_λ be the brightness of the homogeneous light which needs to be added to secure a just perceptible color; let B_W be the brightness of the constant white field; and let P_λ be the minimum perceptible colorimetric purity. Then

$$P_\lambda = \frac{B_\lambda}{B_W} \qquad [8]$$

and represents the definition of least perceptible colorimetric purity. Since the amount of "color" added is assumed constant, the quantity B_λ which has to be added to furnish this color is inversely proportional to the saturation S_λ. This may be written

$$B_\lambda = \frac{k}{S_\lambda} \qquad [9]$$

and can be introduced into equation [8]. The equation now becomes

$$P_\lambda = \frac{K_P}{S_\lambda} \qquad [10]$$

in which $K_P = k/B_W$ since B_W is kept experimentally constant. In other words the minimum perceptible colorimetric purity as determined by Priest and Brickwedde is inversely proportional to the saturation as determinable from the values of the primaries V_0, G_0, and R_0.

Fig. 4 shows the results obtained from V_0, G_0, and R_0 in terms of equations [6] [7] and [10] when $K_P = .001$. Included in Fig. 4 are the average data of Priest and Brickwedde kindly supplied to me by Dr. Priest. It is apparent that the curve derived from V_0, G_0, and R_0 has the same general form as that of Priest and Brickwedde. Starting at the left both show a steep rise in the short wave lengths, then a flat part fol-

lowed by a sudden rise and fall, and finally a slow decline in the red which continues to remain at a level several times higher than that at the violet end.

Whether this is an adequate agreement with the measurements depends on what the individual variations in such measurements are. The data of Priest and Brickwedde shown in Fig. 4 are an average of two observers. Very recently Dr. Priest has most graciously sent me the separate data for his eye and for that of Brickwedde. These measurements are shown in Fig. 5. From a comparison of Fig. 5 with Fig. 4 it is apparent that the differences between the average data and the theoretical

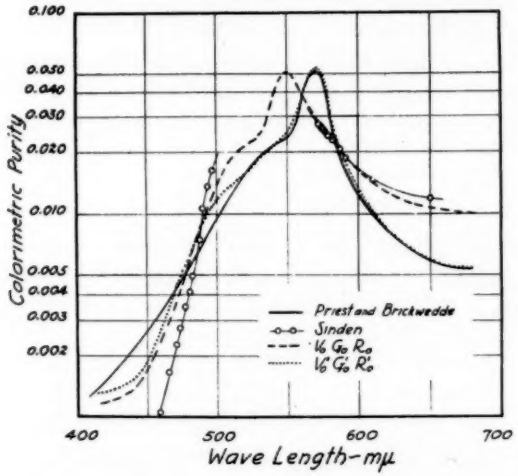

FIG. 4. *Least perceptible colorimetric purity as given by the average data of Priest and Brickwedde, as given from the complementary color luminosity data of Sinden, and as derived theoretically from the cone primaries* V_0, G_0, *and* R_0 *and from the cone primaries* V_0', G_0', *and* R_0'. *Compare these curves with those in Fig. 5.*

curve derived from V_0, G_0, and R_0 are of the order of magnitude to be expected from such individual measurements as are shown in Fig. 5.

An additional index to the possible range of individual variation may be secured by a comparison with the saturation function derived from completely independent measurements such as those describing the relative luminosities of spectral complementaries. It will be recalled that the relative luminosities of a pair of spectral complementaries vary in a very definite way with the wave length. Following the original suggestion of Helmholtz we suppose these differences in luminosity to cor-

respond to differences in saturation of the lights of different wave length. Since the amount of "color" which is contributed by each member of a complementary pair must be the same, then according to this idea the relative luminosity required of each member of a complementary pair should be inversely proportional to its saturation. Thus the relative luminosities of spectral complementaries as measured by Sinden and given in Table 1 are directly comparable with the colorimetric purity data of Priest and Brickwedde. The values L_1 and L_2, multiplied by a factor (0.00038) to bring them to the same order of magnitude as the other measurements, have therefore been plotted in Fig. 4. It is at once

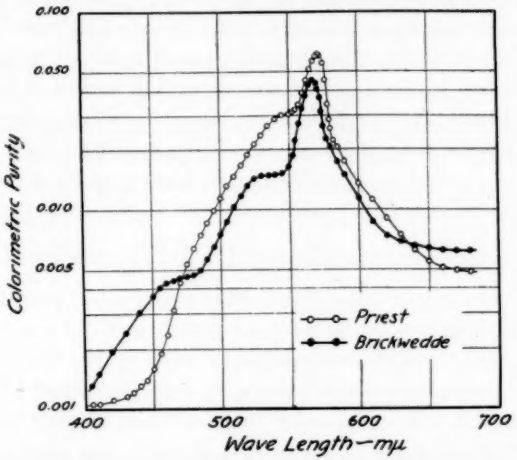

FIG. 5. *The individual measurements of least perceptible colorimetric purity by Priest and Brickwedde. Compare the range of individual variation shown here with the differences between measurements and theory. Note especially Priest's measurements between 400 and 500 mμ and compare them with the theoretically derived curves in Fig. 4.*

apparent that the colorimetric purity function derived from Sinden's data is essentially similar to that derived from V_0, G_0, and R_0, and to the data of Priest and Brickwedde. Because of the nature of spectral complementaries the critical middle portion of the curve is missing. But enough is available to show that the curve from V_0, G_0, and R_0 probably differs only as an individual variation from both Sinden's data and from Priest and Brickwedde's data.

Some concept of the nature of this individual variation can be gained by considering the change that would be required in the color system $V_0G_0R_0$ in order to give an exact reproduction of the average data of

Priest and Brickwedde. This may be illustrated by an examination of the color system $V_0'G_0'R_0'$. These cone primaries are made up according to the equations

$$V_0' = .042v_0 + .721g_0 + .240r_0 \quad [11]$$

$$G_0' = .010v_0 + .738g_0 + .276r_0 \quad [12]$$

$$R_0' = .004v_0 + .605g_0 + .365r_0 \quad [13]$$

and are shown in Fig. 3.

Since the color system $V_0'G_0'R_0'$ is composed of v_0, g_0, and r_0 it describes color mixture data exactly as well as does the system V_0, G_0, and R_0. Also its spectrum visibility curve is much like that of V_0, G_0, and R_0, and falls well within the range of normal observers studied by Gibson and Tyndall, by Ives, and by others. The reciprocal of its saturation is shown in Fig. 4. The curve is almost identical with the average data of Priest and Brickwedde. If it were necessary, an even better approximation could be secured; all that is required is the making of many tedious computations.

IV. Hue Discrimination and Excitation Curves

The last property of color vision that needs to be considered is hue discrimination. Returning to the cone primaries V_0, G_0, and R_0 we may derive from them hue discrimination in terms of the idea (8) that the changes in hue which the spectrum shows are connected with the relative changes which the three color receptors show in their spectral characteristics. Helmholtz (8) assumed a non-linear and quite complicated relation between hue and color receptors, and in order to derive the even meager quantitative data available in his day (18), he had to invent a set of primaries which were neither probable nor useful (5). I shall therefore use a simple and direct formulation in terms of the primaries V_0, G_0, and R_0.

Let us suppose that a minimum hue change at constant brightness will be determined by the way in which the two most rapidly changing cone primaries vary with regard to each other. In other words let us assume that the equations

$$\frac{dH}{d\lambda} = \frac{d(V_0 - G_0)}{d\lambda} \quad [14]$$

$$\frac{dH}{d\lambda} = \frac{d(R_0 - G_0)}{d\lambda} \quad [15]$$

describe the way in which the hue H changes with wave length λ in terms of V_0, G_0, and R_0. Equation [14] describes this relation for $\lambda < 550$ $m\mu$ whereas equation [15] for $\lambda > 550$ $m\mu$.

In order to relate these ideas to the quantitative data of hue discrimination, we must remember first, that what has actually been measured is not a differential but a finite difference; and second, that Laurens and Hamilton, for example, specifically measured a wave-length distance $\Delta\lambda_C$ necessary for a minimal difference in hue ΔH, rather than the reverse. This difference in hue, ΔH, therefore represents a constant difference in the composition of the two perceptibly different hues in the amounts of V_0 and G_0 or of R_0 and G_0 which they contain at constant brightness. This may be related to a difference in the number of cones of each species functional for the two hues.

In the present formulation hue differences are made to correspond to differences in the way two of the cone primaries change. It is likely that the third primary also enters here. I have retained the simple derivation for the present because of obvious computational reasons.

Converting differentials to finite differences and writing $\Delta H = K_H$, we change equations [14] and [15] into

$$\Delta\lambda_C = K_H \frac{\Delta\lambda}{\Delta(V_0 - G_0)} \qquad [16]$$

$$\Delta\lambda_C = K_H \frac{\Delta\lambda}{\Delta(R_0 - G_0)} \qquad [17]$$

in terms of which the experimentally determined distance $\Delta\lambda_C$ along the spectrum required for a constant hue difference is proportional to the distance $\Delta\lambda$ which one has to move on the curves in Fig. 3 to yield a constant value of $\Delta(V_0 - G_0)$ or $\Delta(R_0 - G_0)$.

The procedure for making the calculation is as follows. There is first determined from Table 3 the values of $V_0 - G_0$ between 400 $m\mu$ and 550 $m\mu$ and for $R_0 - G_0$ between 550 $m\mu$ and 700 $m\mu$. The values in the two sets pass continuously from one to the other, and are shown as a continuous curve in Fig. 6. Using this curve one determines the difference between the ordinates of any two values λ_1 and λ_2 which are 10 $m\mu$ apart. This yields a set of values of $\Delta(V_0 - G_0)/10$ or $\Delta(R_0 - G_0)/10$ throughout the spectrum. The reciprocals of these numbers when multiplied by K_H give $\Delta\lambda_C$ for the point midway between λ_1 and λ_2. In securing $\Delta(V_0 - G_0)$ and $\Delta(R_0 - G_0)$ one may start at any value of λ in Fig. 6. But if one of the sharp breaks in the curve comes between λ_1 and λ_2 one must reckon

$\Delta(V_0-G_0)$ or $\Delta(R_0-G_0)$ from λ_1 to the break and then from the break to λ_2. The breaks are of no special significance. They represent only a sharp change in the sign of the slope of the curve; the actual magnitudes of V_0-G_0 and R_0-G_0 change smoothly through them.

The results of such a computation from V_0, G_0, and R_0 for values of λ_1 and λ_2 as 400 and 410 $m\mu$, 410 and 420 $m\mu$, and so forth, are given in

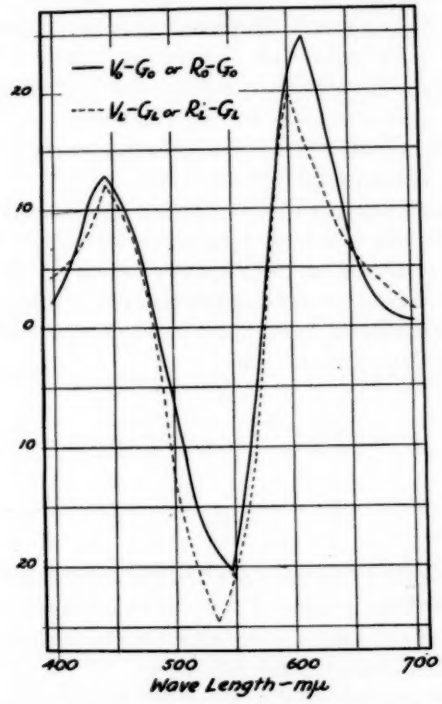

FIG. 6. *Values of V_0-G_0 or R_0-G_0 and of V_L-G_L or R_L-G_L from which theoretical hue discrimination curves are derived.*

the curve in Fig. 7. Here $K_H=0.35$. There are also included in Fig. 7 the hue discrimination data for Laurens' eye and for Hamilton's eye taken from the data of Laurens and Hamilton. These two curves do not represent the extremes of individual variation shown by the observers in this particular investigation; they are typical rather than the reverse. Moreover even these two trained observers give different curves at different times and with different methods of making measurements.

Fig. 7 then shows that the color system $V_0G_0R_0$ gives a hue discrimination curve which has the same form and magnitude as are found experimentally. The theoretically derived curve has the same number of maxima and minima, and these maxima and minima occur in about the same places as those found experimentally. The curve as a whole differs no more from the hue discrimination data of any one observer than one observer differs from another.

No very great change is necessary in the cone primaries in order to secure an exact reproduction of a given set of hue discrimination data, for

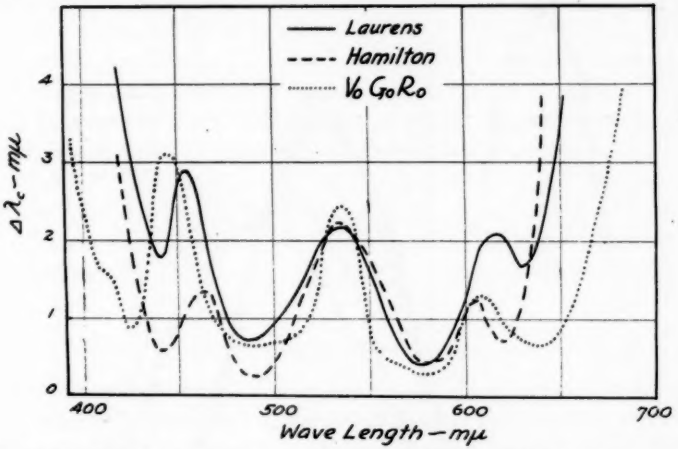

FIG. 7. *Hue discrimination as measured by Laurens and Hamilton for their own eyes, and as derived theoretically from V_0, G_0, and R_0. The hue discrimination function derived from V_L,G_L, and R_L coincides with the curve for Laurens' eye.*

example those of Laurens' eye. This change apparently has to include an alteration in the values of the excitation curves.

The cone primaries V_L, G_L, and R_L given in Fig. 3 and in Table 3 constitute such a color system. They are given by the equations

$$V_L = .032v_L + .533g_L + .401r_L \quad [18]$$

$$G_L = .007v_L + .620g_L + .402r_L \quad [19]$$

$$R_L = .006v_L + .489g_L + .541r_L \quad [20]$$

where v_L, g_L, and r_L are the required excitation curves.

From these cone primaries the values of $(V_L - G_L)$ are found for $\lambda < 510$ $m\mu$ and of $(R_L - G_L)$ for $\lambda > 510$ $m\mu$. The results are given in Fig. 6. From this curve the magnitudes $\Delta(V_L - G_L)/10$ and $\Delta(R_L - G_L)$

/10 are derived as before, and their reciprocals taken. When these reciprocals are multiplied by $K_H = 0.523$ there is secured a series of values of $\Delta\lambda_C$ constituting a hue discrimination function which is a perfect replica of that given in Fig. 7 for Laurens' eye. The reason for this precise duplication is that the curves V_L, G_L, R_L and of course v_L, g_L, r_L were constructed from Laurens' data by the reverse of the procedure here described.

The functions v_L, g_L, and r_L of which the color system V_L, G_L, R_L is composed are given in Fig. 8. Included in Fig. 8 are the standard excitation

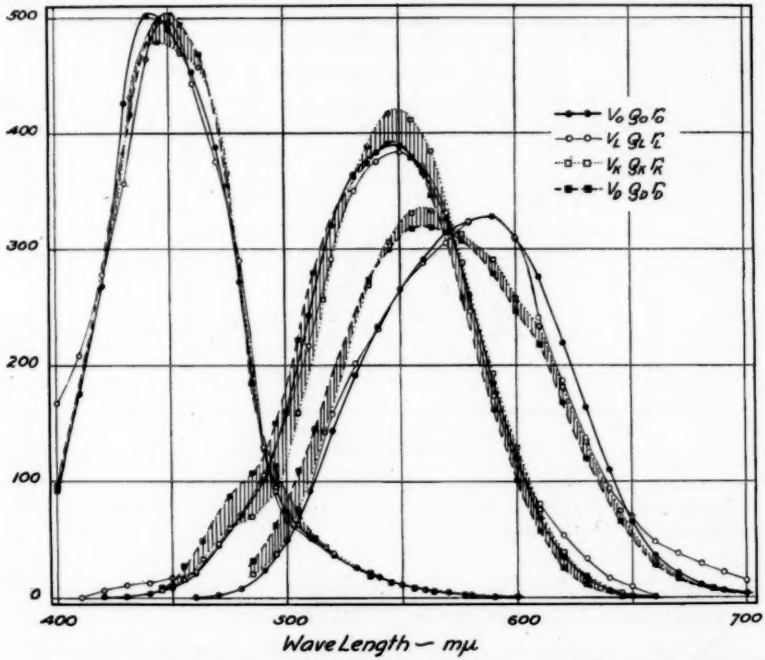

FIG. 8. *Excitation curves for sunlight. The set $v_0g_0r_0$ is the one adopted by the Optical Society. The sets $v_Kg_Kr_K$ and $v_Dg_Dr_D$ are the original ones of Koenig and Dieterici for their own eyes; their original ordinates have been multiplied by 0.035 to make them comparable to the other curves in this figure. The set $v_Lg_Lr_L$ is the one assumed to give the cone primaries V_L, G_L, and R_L which yield a hue discrimination function exactly reproducing the data for Laurens' eye. The points for Koenig and for Dieterici have been connected with vertical lines to emphasize the individual variation possible in such measurements. To be compared with the differences between Koenig and Dieterici are the differences between the set $v_0g_0r_0$ and the set $v_Lg_Lr_L$.*

curves v_0, g_0, and r_0 and the actual excitation curves as derived by Koenig and Dieterici (19) for their own eyes. The values of Koenig and Dieterici have been multiplied by 0.035 to make them comparable with

the standard values in Table 2. It is apparent that v_L, g_L, and r_L differ little more from the standard excitation curves than do the individual curves of Koenig and Dieterici from each other. The r_K and r_D curves of Koenig and Dieterici are not directly comparable with the r_0 and r_L curves; the former refer to 670 $m\mu$ as a standard while the latter refer to the extreme red of the spectrum as a standard. The point of interest for us however is the magnitude of the differences between Koenig and Dieterici in comparison to the differences between the standard excitation curves and those required to yield Laurens' hue discrimination data perfectly.

It may not be amiss to point out that in building the v_L, g_L, and r_L curves from the data for Laurens' eye I found it impossible to move the maximum of the v_L curve any further toward the violet end of the spectrum. It is therefore not without interest that a comparison of Wright's recent and extensive measurements (29) with the older ones of Koenig and Dieterici (19), leads one to judge this position of the maximum of v_L as more nearly correct than that of v_0, v_K, and v_D. Wright attributes the differences in this region between his results and those of Koenig and Dieterici to his higher luminosities, and to his greater care in eliminating stray light.

V. COLOR SENSATIONS

The present treatment of color vision has been confined to data which are available in quantitative, numerical form. The sensations associated with securing these data have not been presented because they are not necessary in the description. The data we have used record measurements of wave lengths and of energies under such conditions that the subject is required merely to record whether the two halves of a visual field are the same or different. The data of color mixtures are such measurements: two fields must be made to look exactly alike to the eye even though their compositions are quite different. The measurements of brightness require two intensities to be varied until two sides of a field are identical. Even heterochromic brightness comparison is no longer a problem because it can be made by the flicker method or by the step-by-step method into which differences of color do not enter. Complementary color measurements involve making one field composed of two monochromatic frequencies match exactly another field illuminated with the total visible light from a black body at 5000°K or with Abbot-Priest sunlight or any other standard source. On the other hand, determinations of hue discrimination consist of the reverse process of

starting with equal fields and changing the wave length of one side until the observer declares that even by varying their intensities the two fields cannot be made to look alike. The same is true of colorimetric purity measurements. Homogenous light is added to one side of a photometric field until the observer says the fields no longer match.

Since the qualities of the sensations do not enter into the data they need not be introduced into the theoretical derivations from V_0, G_0, R_0 or the other cone primaries. All that is required is that there be three cone primaries and that the sensory effect produced when each one is activated be different qualitatively from the others.

Nevertheless these specific sensations do exist, and they have so long been part of the problem of color vision that they cannot be ignored. It is of course not possible to describe with any semblance of certainty the pure, individual, primary sensations associated with the separate stimulation of each of the three species of cone. Very likely the R sensation would be a red with no yellow and no blue tinge to it; probably it would resemble the sensation associated with wave lengths between 650 and 700 mμ, but it would considerably exceed such a sensation in saturation. The hue of the G sensation would probably be like that produced by the region 500–505 mμ, but enormously more saturated.

While one may deal with a V curve in the computations, there are many reasons (5) for considering only a B (blue) cone process. The B sensation would then resemble in hue that produced by about 470 mμ, but would also be much more saturated. The designation V comes about because the B process always seems to be accompanied by a small amount of the R process which is called into play under spectral conditions identical with those of the B process.

I have previously (5) given an interpretation of this situation and need go no further into it at present. It is mentioned here because it furnishes the physiological reason for the position of the crossing of the V_0 and R_0 curves. Since the purest green sensation occurs at about 500–505 mμ, this should be the point where the other two primaries are equal. It is here then that the B process equals the R process. But obviously it cannot be the place where V_0 and R_0 cross because V_0 already contains some of the R process in it; therefore V_0 and R_0 must cross farther toward the red end of the spectrum. The amount of the R process which accompanies the B process then determines the precise crossing point of V_0 and R_0 or of the other corresponding cone primaries.

VI. MATHEMATICAL INTERRELATIONS

After this inadequate but necessary excursion into the sensory qualities associated with color vision, let us return to the numerical data. All the computations and figures which have been presented merely serve to show that it is possible on the basis of certain ideas to relate quantitatively to one another the different aspects of normal color vision. The problems of abnormal color vision I have already discussed in connection with these ideas; that discussion still stands (5). The exact form of the ideas which I have suggested is far from final. They have been presented concretely in numerical shape, because only in such a way can they be studied and evaluated. The ideas themselves and their particular form must however be considered merely as quantitative experiments in thinking about color vision.

Perhaps the whole matter may be summed up in the most general terms. Taking the standard excitation curves v_0, g_0, and r_0 as a basis, there may be built up by a given series of linear and homogeneous transformations a set of functions V_0, G_0, and R_0 which yield precisely or approximately the various data of color vision. Therefore v_0, g_0, and r_0 themselves yield the same things. One may thus describe the different aspects of color vision in two ways, either in terms of v_0, g_0, and r_0 or in terms of V_0, G_0, and R_0.

The visibility of the spectrum is given by the expression $V_0+G_0+R_0$ or by its equivalent $3(.015v_0+.547g_0+.438r_0)$. Hue discrimination is derived from the slope of the curves formed by plotting V_0-G_0 and R_0-G_0 against wave length. But since V_0, G_0, and R_0 are themselves functions of v_0, g_0, and r_0 as shown in equations [1], [2], and [3], then for V_0-G_0 and R_0-G_0 one may write equivalent expressions composed of v_0, g_0, and r_0. Such expressions are given in the second column of Table 4. Exactly the same thing is true of saturation. Saturation is defined by the two ratios $(V_0+G_0-2R_0)/(V_0+G_0+R_0)$ and $(G_0-R_0-2V_0)/(V_0+G_0+R_0)$. In terms of these ratios saturation is related to minimum perceptible colorimetric purity data and to the luminosities of spectral complementaries. But since V_0, G_0, and R_0 may each be written as functions of v_0, g_0, and r_0 the two saturation ratios may be similarly written. The two corresponding expressions are given in Table 4.

All the relevant data of color vision are thus interrelated and may be derived from v_0, g_0, and r_0. However, a series of relations such as those given in the second column of Table 4 are both empirical and arbitrary. The mathematical expressions involving v_0, g_0, and r_0 possess no apparent physiological or physical meaning; and the values of the coeffi-

TABLE 4. *Relation of the properties of color vision to the excitation curves and to the hypothetical cone primaries.*

Property of color vision	In terms of v_0 g_0 r_0	In terms of V_0 G_0 R_0
Color mixture	$f\begin{pmatrix}.015v_0\\.547g_0\\.438r_0\end{pmatrix}$	$f\begin{pmatrix}V_0\\G_0\\R_0\end{pmatrix}$
Luminosity	$3(.015v_0+.547g_0+.438r_0)$	$V_0+G_0+R_0$
Saturation	$\dfrac{.013v_0+.070g_0-.081r_0}{.015v_0+.547g_0+.438r_0}$	$\dfrac{V_0+G_0+R_0-3R_0}{V_0+G_0+R_0}$
	$\dfrac{-.018v_0-.010g_0+.043r_0}{.015v_0+.547g_0+.438r_0}$	$\dfrac{V_0+G_0+R_0-3V_0}{V_0+G_0+R_0}$
Hue discrimination	$\dfrac{.025v_0-.050g_0-.004r_0}{-.010v_0-.130g_0+.120r_0}$	$\dfrac{V_0-G_0}{R_0-G_0}$

cients and the signs in front of v_0, g_0, and r_0 have no rational basis. On the other hand, if a set of functions like V_0, G_0, and R_0 is formulated, then two things happen. In the first place, as the third column of Table 4 shows, all these aspects of color vision are derivable by the simple addition or subtraction or division of the values of V_0,G_0, and R_0 themselves without any arbitrary coefficients; and in the second place, these various manipulations are rational procedures which possess meaning in terms of an hypothetical receptor mechanism.

SUMMARY

Assuming Young's trireceptor hypothesis as a basis for a theory of color vision, it is possible to show that the five aspects of normal color vision which have been accurately measured are quantitatively related to one another, and may all be derived according to certain rules of computation from the spectral characteristics of the three primary receptor processes.

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(29) Wright, W. D. *A Re-determination of the Trichromatic Coefficients of the Spectral Colours.* Trans. Opt. Soc., *30*, No. 4, p. 141; 1928–29.
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A COLORIMETER FOR USE WITH DISC MIXTURE*

By Dorothy Nickerson

[Bureau of Agricultural Economics, United States Department of Agriculture, Washington, D. C. Received March 24, 1931]

In order to measure the color of agricultural products—hay, cotton, grains, fruits and vegetables, etc., a colorimeter has been developed with the cooperation of Mr. Carl W. Keuffel of the Keuffel & Esser Company.

It employs a method different from other colorimeters and provides several new, and, to us, very useful features that may be adapted for use in fields other than agriculture.

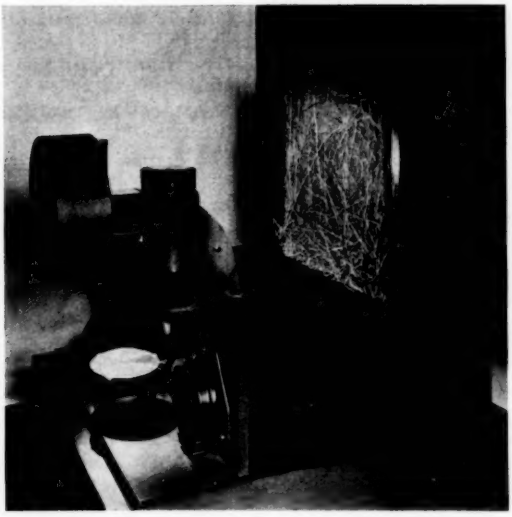


Fig. 1. *Colorimeter for use with disc mixture set up for measuring a 12 inch diameter area of hay.*

First, the method of measurement, by the use of disc mixture of Munsell papers, permits the expression of results in terms which adequately approximate the psychological attributes, hue, brilliance, and chroma.[1] Second, the instrument may be adjusted at will to measure either a large or a small area (this is often necessary in order to obtain a repre-

* Paper presented before the Optical Society, February 27, 1931, in New York City.

[1] For a discussion of advantages and precautions for using the Munsell notation in this regard, see p. 17, also footnote on same page, of Technical Bulletin No. 154, U.S.D.A., *A Method for Determining the Color of Agricultural Products*

sentative sample). Third, it measures the average color of a highly variegated surface. And fourth, it has a unique method of illumination by cross lighting.

Fig. 1 shows the latest model of the instrument as it is set up to meas-

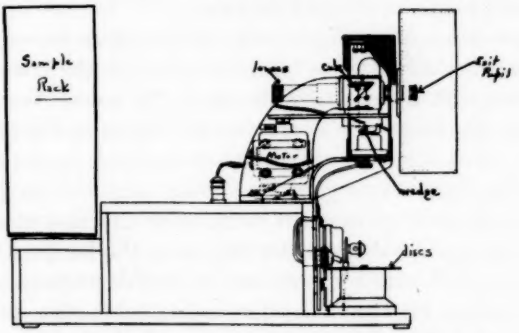


FIG. 2. *Diagram of the side view of colorimeter illustrated in Fig. 1.*

ure hay. The area measured is twelve inches in diameter. The hay is seen in the eyepiece as a uniform color which can be matched easily to the color of the discs. The instrument may be adjusted for measuring an area four inches in diameter by the removal of one lens. The area can be

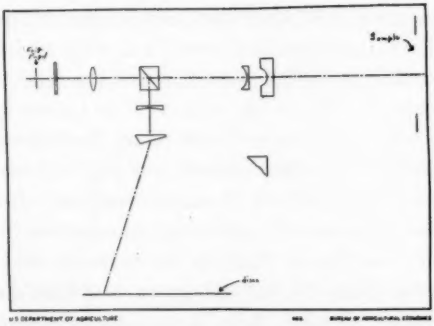


FIG. 3. *Optical system for colorimeter using disc mixture for comparison standard.*

futher decreased if desired. Samples may be placed under glass and any liquid or granular substance may thereby be measured.

Fig. 2 is a diagram of the side view of the instrument. The light from the sample is brought through the series of lenses, through the photometric cube, to be focused on the exit pupil. The light from the stand-

ard comparison discs is mixed by a revolving wedge and directed to the photometric cube where its direction is changed, to be focused also upon the exit pupil. The sample field is uniform in color since the image seen is that of the cube, not of the sample itself.

Fig. 3 is a diagram of the optical system.

The illumination is supplied by two lamps which are so placed that they are in a horizontal plane with the center of the sample and in a vertical plane with the center of the discs. The use of 50-volt prefocus movie projection lamps such as are used for home sets was Mr. Keuffel's suggestion. These lamps have four coiled filaments in the same plane. Naturally, the light that is given off at right angles to the plane of the four filaments is greater than that in the same direction when the lamp is rotated through 90 degrees. By adjusting the lamps, the bases of which are provided with a slot and screw for this purpose, the light on the sample surface may be made equal to that on the disc surface.

This method of light adjustment provides for darkening such samples as are too light to be measured with available discs, such samples as butter and angel cake, and lightening such samples as may be too dark to measure, such as prunes and raisins.

The instrument is easy to operate, and equally easy to calibrate.

If there should be reasons that make it seem undesirable to anyone to express the results of measurement in terms approximating the psychological color attributes, then the instrument still provides a large sample field for measurement and may be used as a photometer by the substitution of black and white discs of which the reflection is known. If it is more important to know the reflection or transmission at definite wave length bands than it is to know what the color looks like, such filters as those of the Wratten "monochromatic" set may be employed, and the instrument converted to a simple analyser, similar in result to one or two of the photoelectric cell instruments now in use. Or, if it is unnecessary to use as many filters as the seven in this set, the instrument may be fitted with selected red, green, and blue glasses, the measurements being made through them by matching the samples with black and white discs.

For use in measuring liquids, one of two methods may be selected. If only a small amount of the liquid is available, it may be placed in a glass cell which can be supplied to fit over the end of the optical tube. Or the liquid may be placed in a container in the usual position. In each case, a standard neutral of known reflectance must be placed at the usual position and viewed through the liquid.

COLOR MEASUREMENTS IN PSYCHOLOGICAL TERMS*

By Dorothy Nickerson
[Bureau of Agricultural Economics, United States Department of Agriculture, Washington, D. C. Received March 14, 1931]

Presenting color data to the layman is a task that requires study. When a single commodity is highly standardized for color, with a group of highly trained classers or graders, it is desirable to express measurements of these commodities in terms that can be correlated with the grader's recognition of color differences. For that reason, in our color work pertaining to commodity standardization and utilization in the Bureau of Agricultural Economics of the Department of Agriculture on hay, cotton and other products, we selected the Munsell notation for the expression of results. The method of measurement, employing the instrument previously described—or, more simply, with a set of color discs spun on a top and matched to the sample—permits the expression of results in terms which adequately approximate[1] the psychological attributes referred to in the Colorimetry Report of this society as hue, brilliance and saturation.

You will recall the relation of the three color attributes, a color solid in which brilliance is the vertical dimension, chroma or saturation the horizontal dimension, with hue shown in an angular direction. (Fig. 1). The first figure indicates the possibilities of the notation. Brilliance, for example, may be expressed in a series of 11 steps from 0 to 10, or the steps may be subdivided decimally to give 100 equal steps to the eye, or even 1,000 if they are necessary. Hue and chroma may be subdivided in the same way.

Because of uniform steps the notation used provides a particularly convenient method of plotting the information. For example, for standardization purposes the color of evaporated milk[2] is of importance. Fig. 2 illustrates the regularity of color change. Brilliance is plotted on the vertical axis against chroma on the horizontal axis. Hue is indicated by the figures on the curve. As the grade of the milk becomes lower the hue becomes redder as indicated by the change from 5.93Y back to 0.07Y, the brilliance becomes less, and the chroma becomes greater. Suppose now, that for some reason it is desirable to study the relative

* Paper presented before the Optical Society, Feb. 27, 1931, in New York City.

[1] For formulas, with precautions regarding their use, reference may be made to Technical Bulletin 154, U.S.D.A., *A Method for Determining the Color of Agricultural Products*, by Dorothy Nickerson.

[2] *Color of Evaporated Milks*, by Webb and Holm, J. Dairy Science, *13*, No. 1, 25 to 39; Jan., 1930.

color differences of two very different products, as the relatively light, weak yellows of condensed milk with the dark greenish yellow of canned

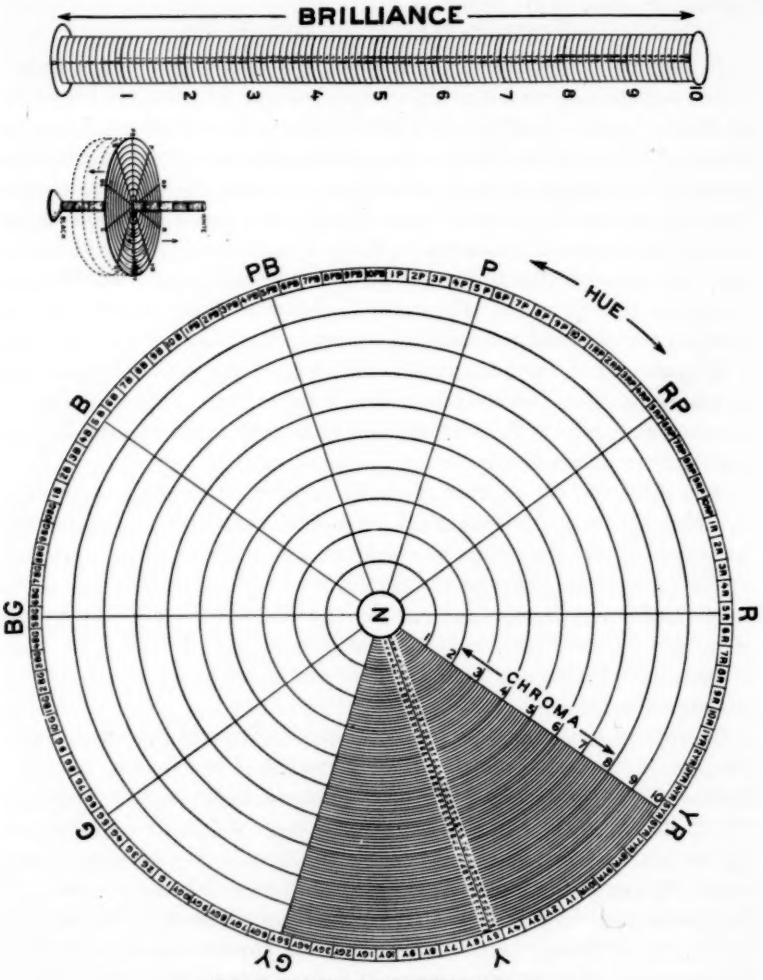


FIG. 1. *Notation for hue brilliance chroma.*

spinach. The relative differences are indicated in Fig. 3. It may be noted that grade qualities are indicated by different color changes. While the lower grades for condensed milk become redder, darker and stronger, the lower grades of spinach show no definite hue change, but

become lighter and stronger. While the milk ranges in brilliance from about 6.5/ to 8.5/, the spinach ranges from about 2/ to 3.5/. While there is a regular hue progression in the milk samples, there seems to be no such hue order in the spinach.

Sometimes, as in the case of alfalfa hay, it is found that one color factor is sufficient for grading purposes. Fig. 4. For example, in making a chart for converting color measurements into terms of what the trade calls "per cent natural green," the color measurement, in terms of three factors, hue, brilliance and chroma, was correlated against grade as estimated by several inspectors. The correlation[3] was $P = .973$, with hue contributing all but a very little to the total, giving evidence that for

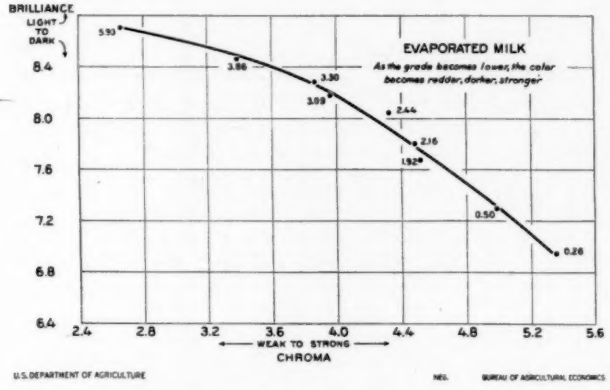


FIG. 2. *Color curve for different samples of evaporated milk illustrating regularity of color change from high to low grade.*

practical use a chart converting the color measurements into grade may be based upon hue alone. Since hue alone seemed to be the important color factor, the chart constructed was based upon moving averages of the alfalfa samples plotted with hue against "percent natural color." Since 75 percent, 60 percent and 35 percent are the limits for grade, the lines shown on the curve separate the grades on the basis of hue. Data for other products may be treated similarly.

In making hay measurements, practical limits of accuracy have been established. For example, there are instruments now in use in several

[3] Mordecai Ezekiel, 1924, *A Method of Handling Curvilinear Correlation for Any Number of Variables*. J. Amer. Statis. Assoc. (n. s. 148) *19*: (431)–453, illus.

Mordecai, Ezekiel, 1930, *Methods of Correlation Analysis*, John Wiley & Sons, 1930.

different offices. They are operated by the men in charge of hay inspection, tested, of course, for color vision, yet not trained technicians who may be expected to make color matches with the greatest precision. As

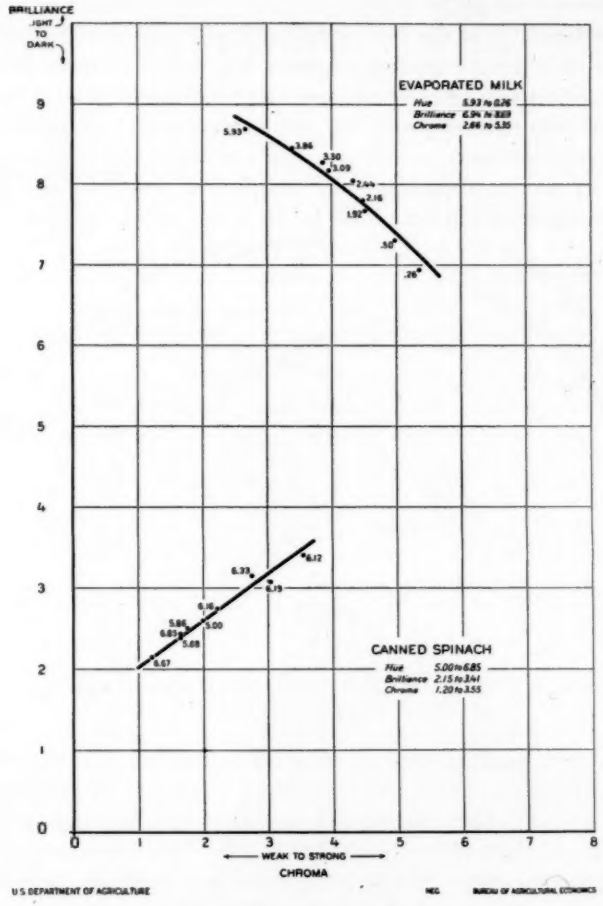


FIG. 3. *Comparison of color difference of two products, one the relatively light, weak yellows of evaporated milk, the other the dark greenish yellow of canned spinach.*

a result of experience, we may expect that about 90 percent of the readings on a single sample by such men will fall within 0.5 of a hue step (1 in a total of 200), within 0.1 of a brilliance step (1 in a total of 100), and 0.15 of a chroma step. Results of a statistical analysis of measure-

ments on six samples is discussed below. Each sample was read by four observers, three of whom were being taught to use the instrument described in the previous paper. Each observer made two readings on each sample before the sample was removed from the instrument. These six samples are selected from sixty-four because they are the only six which were replaced in the instrument and read for a second time by the same four observers. Although results on only six samples are given, the remainder of the sixty-four were comparable to these. By averaging the probable error of a single observation (four observers making measurements on six samples, on both the top and bottom sides of each sample, making a total of twelve sets of observations) according to the formula

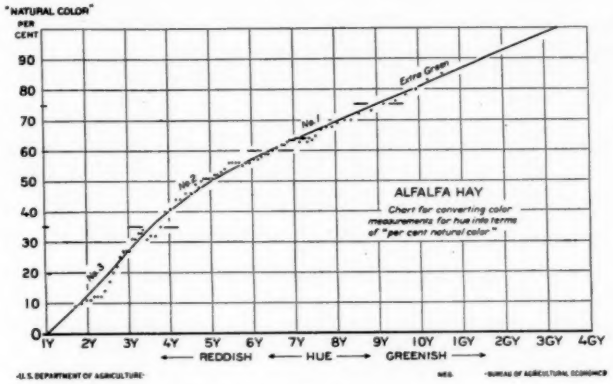


FIG. 4. *Color "conversion chart" for alfalfa hay.*

P.E. $=.6745\sqrt{\Sigma v^2/n-1}$ (v representing the variation of a single observation from the mean of 4, the number (n) of observations in each set of measurements) the first readings gave an average of .224/.020/-.070 for probable errors of hue/brilliance/chroma readings. A second set of readings by the same four observers gave .167/.020/.049. Taking the second set of figures, which, although they are smaller than the first set, is justifiable because three out of four of the observers were using the instrument for the first time and the second set of measurements should be more representative than the first, the figures representing 6 times the probable error are 1.00/.12/.30 for hue/brilliance/chroma. Note should be made that the approximate ranges expected as a result of experience in hay color measurement as quoted in a previous paragraph, are approximately three times the probable error for hue and chroma and five

times for brilliance. In addition to this study, a comparison has been made of hue readings on sixty-eight Johnson hay samples and fifty Prairie hay samples read on the first and second models of the instrument. Of course these figures include any differences that there may be between instruments as well as between readings, but it will indicate the closeness which may be expected. The mean of the hue differences between observations made on two instruments for sixty-eight Johnson samples is .317 with a P.E. of $\pm .150$, that of the fifty Prairie samples is .329 with a P.E. of $\pm .213$

However, in measuring several seed samples in the laboratory some time ago, the actual differences were so reduced that the standard deviation of measurements on five lots of seed, each divided into five samples, with three measurements made on each sample, averaged 0.15 of a hue step, less than one-third of the variation reasonably expected in our hay work, .004 of a brilliance step (figured on readings to one decimal place only so that although it is considerably smaller than the figure for hay we cannot make a direct comparison) and 0.04 of a chroma step, almost one-quarter of the variation expected. As may be seen from Table 1, the differences between lots is extremely slight, and in identifying samples, the measurements had to be made as precisely as possible.

TABLE 1. *Color measurements on seed. November 1930*

Five lots of seed each lot divided into five samples with three readings made on each sample. Color measurements in terms of hue/brilliance/chroma.

Average of lot	Standard deviation ($\pm$)
1.63/4.3/3.22	.13/.02/.04
1.85/4.5/3.73	.14/.00/.06
2.06/4.5/3.75	.20/.00/.04
1.13/4.4/3.51	.15/.00/.03
2.04/4.4/3.44	.15/.00/.02

In a series of seventy-five sets of cotton standards put up by trained cotton classers and very carefully reviewed, the colors at several positions within certain so-called "flat" boxes (that is, boxes purporting to be of the same color throughout) were measured and the standard deviation found for the color differences. If our own measurements are relatively free from errors these figures indicate very nearly the highest accuracy for color matching of a non-uniform surface by the trained but unaided eye, since the classers put up these standards with no instrument; their only reference is the standard box which they have for com-

parison. Table 2 has, in the first column, the mean of hue, brilliance, and chroma measurements for three groups of seventy-five samples selected from three different grades of cotton. The three means in any one group

TABLE 2. *Color measurements on cotton 1930–31*

Each average represents seventy-five samples put up by eye to match a standard sample of cotton. The color measurements are in terms of hue/brilliance/chroma.

	(1) Average	(2) Standard deviation of readings on seventy-five samples ±	(3) Mean of differences in readings made on each sample by a single observer with P.E. of that mean	(4) Mean of P.E.'s for single observations by a single observer
Three series from the same grade.	9.88/7.86/3.12	.20/.07/.06		
	9.84/7.84/3.12	.24/.06/.07		
	9.87/7.89/3.11	.23/.07/.07		
Three series from the same grade.	8.63/7.51/3.18	.15/.08/.09	.17/.02/.05± .085/.013/.030	.079/.011/.024
	8.58/7.46/3.17	.13/.10/.05	.16/.02/.05± .079/.013/.030	.075/.017/.024
	8.61/7.53/3.17	.14/.08/.08	.13/.02/.05± .083/.012/.032	.064/.010/.023
Three series from the same grade.	10.48/7.23/0.70	.38/.12/.04	.65/.02/.04± .378/.011/.026	.307/.010/.017
	10.50/7.24/0.70	.44/.11/.05	.60/.02/.04± .335/.011/.029	.280/.009/.019
	10.51/7.24/0.71	.42/.08/.05	.64/.02/.04± .333/.011/.028	.292/.011/.020

of three sets of measurements should be the same if the cotton is truly uniform in all the positions indicated. They are very close within each group, as can be seen from the figures. The dispersion of colors about the mean is measured by the standard deviation in the second column. This figure, however, represents not only the actual color difference between the samples but includes also the observational variations. If, for example, the errors of observation were of a magnitude comparable to the difference in the samples, such a figure would be of little use in studying the color variations within any one grade of cotton. Therefore, since two observations were made on each sample, the mean of the difference between those readings, with a probable error for that mean, should indicate the relation of the observational error in using the instrument with the variation in the samples prepared as color matches out of single bales of cotton. Such a figure is given in column three of Table 2. For a further comparison, the probable error of each single observation was calculated from the formula P.E. $=.6745\sqrt{\Sigma v^2/n-1}$. The mean of these probable errors is given for several sets of the observations in column four of Table 2.

It will be noted that the standard deviation of the hue readings varies with the size of the average chroma figure. This follows because readings are made in terms of percent area of discs exposed and are never read in

fractions of 1 percent. Therefore, when the chroma is low, there may be only 4 percent of the *YR* disc and 5 percent of the *Y* disc exposed: when the chroma is higher there may be 14 percent of *YR* and 20 percent of *Y* exposed. Since hue is calculated from the relative amounts of the colors exposed, 1 percent out of a total of nine will give a larger hue variation than 1 percent in a total of thirty-four. It is also true that small hue differences are not as easily seen at the lower chromas.

The tables and graphs indicate the usefulness of color measurements expressed in psychological terms, even though those terms may be but approximate. The very small differences that are measurable may be mentally visualized by reference to the Munsell charts—often they are smaller than one-tenth of the differences illustrated in those charts—and this mental visualization of color differences serves admirably to relate color measurements to a layman's experience of color.

THE WORK OF THE TEXTILE COLOR CARD ASSOCIATION*

By Margaret Hayden Rorke†
[Textile Color Card Association, 200 Madison Avenue, New York, N. Y. Received July 3, 1931]

Until 1914 American textile and allied industries depended upon European sources for information regarding colors and for guidance in choosing them. To meet the emergency created by the war, leading representatives of the silk, wool, cotton, and millinery industries joined in supporting the foundation of the Textile Color Card Association of the United States, Inc.

For many years there had existed a crying need for color standardization. A common nomenclature was needed, so that staple colors, which represent approximately 85 percent of the entire consumption, would be known under standard names and numbers to be used by dyer, manufacturer and distributor in all branches of the textile trade. Consequently, color standardization was the cornerstone on which The Textile Color Card Association was built.

As one of its principal activities, the Association created the Standard Color Card of America. This card first contained a collection of 106 staple colors. The colors were and are still shown in silk ribbon, which is skein-dyed and woven especially for this purpose, in grosgrain and satin combination, so as to give the dull as well as the luminous value of each color. The ribbons were arranged in flat loops so that a color can be easily matched by slipping it under the ribbon. The entire collection was compiled according to family classification, as far as practical, in order to maintain color harmony and avoid discord.

In order to forecast each season's color development and supply advance information, the Association instituted the Season Color Cards of America. These supplement the Standard Card and are issued each Spring and Fall. While the majority of the colors are novelty shades, created especially for a given season, there are often some staples included and some past season's colors recalled, when they give promise of continued popularity. Staple colors appearing on the season cards are taken from the Standard Card and retain their same name. Each seasonal color is likewise given a name. Besides a name each color has a

* Abstract of paper presented at the special meeting of the Optical Society of America on Colorimetry, February 26, 1931

† Managing Director Textile Color Card Association.

cable number by which a color can be ordered by telegram or cable from any part of the world.

The 8th and current edition of the Standard Color Card of America, issued in 1928, contains 192 staple colors. There are 49 distinct color families, all assembled in harmonious analogy. The families are arranged in groups containing from two to eight gradations of one color. There are thirteen single colors that represent individual types.

Since its establishment in 1915, the Textile Color Card Association of the United States, Inc., has issued over 350,000 color cards. These have been distributed in every state, in Canada, and in 27 other foreign countries. Although the Association was founded primarily for the textile and allied industries, for many years it has also set standards and created the official colors for the hosiery and shoe and leather industries, The Textile Color Card Association is now an international institution with a membership of over 1600, including not only the so-called "Fashion Industries", but all the leading dyestuff producers and dyers, as well as many miscellaneous industries, such as paint, paper, automobile, rubber, carpets, etc., and most of the leading department stores throughout the country.

The Textile Color Card Association links industries together through industrial committees and trade associations, so that constructive seasonal color programs are promoted, color problems adjusted and the economic production of color fostered. Among the Trade Associations cooperating with the Textile Color Card Association in its seasonal color promotion are the Tanners' Council of America, The National Boot and Shoe Manufacturers' Association, the National Shoe Retailers' Association, The National Association of Hosiery and Underwear Manufacturers, The National Knitted Outwear Association, The Associated Dress Industries of America, The Silk Association of America, The Eastern Millinery Association, The National Retail Dry Goods Association, The Industrial Council of Cloak, Suit and Skirt Manufacturers, Inc., and the Wool Institute.

The Association also cooperates very closely with the Department of Commerce and other branches of the Government. It has issued the first official Color Card comprising the official colors of the Arms and Services of the United States Army. The card is supplied by the Quartermaster Corps to each post, camp, and station in the Army, and the purchasing depots use it as the standard for shades whenever any textile articles are required. Through the cooperation of the Department of Commerce and State Department, all the cards issued each year by the

Association are distributed through these two government departments to every American Consul and Commercial Attaché throughout the world.

The Association has established scholarships in three schools, the Philadelphia Textile School, the Lowell Textile School, and the New York Textile High School. Industry needs trained colorists, and it is the ambition of the Association to be one of the means of training men and women who will carry the message of color into our industrial arts, to the end that a higher and finer appreciation of color may be cultivated among the American people.

THE PHOTOGRAPHIC UNIT OF INTENSITY

[Report of the Optical Society of America Committee[1] on the Photographic Standard of Intensity. Received July 1931]

I. Recommendation of the Seventh International Congress of Photography

At the Seventh International Congress of Photography, held in London in July, 1928, the following resolution was adopted (Proceedings, p. 173):

This meeting of the 7th International Congress recommends to the National Committees that the photographic unit of intensity for the sensitometry of negative materials shall be defined as the intensity of a filtered source of radiation having a luminous intensity of one international candle, and produced by a gray body at a colour temperature of 2360°K., together with a selectively absorbing filter made up as follows: Two solutions compounded according to the following formula, the complete filter to consist of a one-cm* layer of each solution contained in a double cell made by using three pieces of borosilicate crown glass (refractive index, $D=1.51$), each 2.5 mm thick.

Solution A

Copper sulphate, ($CuSO_4$, $5H_2O$)	3.707	grm**
Mannite, ($C_6H_8(OH)_6$)	3.707	grm**
Pyridine, (C_5H_5N)	30.0	cc
Water (distilled) to make	1000.	cc

Solution B

Cobalt ammonium sulphate, ($CoSO_4$, $(NH_4)_2SO_4$, $6H_2O$)	26.827	grm**
Copper sulphate, ($CuSO_4$, $5H_2O$)	27.180	grm**
Sulphuric acid (Sp. gr. 1.835)	10.0	cc
Water (distilled) to make	1000.	cc

It is recommended that the foregoing resolution shall come into force as a decision of this 7th International Congress if and when ratified by the National Committees represented at this Congress.

* Tolerance in thickness shall be ± 0.05 mm.

** For practical purposes an accuracy to the second place of decimals is probably sufficient.

(The "Editor's Note" quoted on p. 173 of the Proceedings was not a part of the resolution adopted and is in error, as explained later in this report.)

[1] This committee consists of the following members:

A. C. Hardy, Massachusetts Institute of Technology; H. E. Ives, Bell Telephone Laboratories; Loyd A. Jones, C. E. K. Mees, Eastman Kodak Company; A. G. Worthing, University of Pittsburgh; B. H. Carroll, E. C. Crittenden, Raymond Davis, K. S. Gibson (Chairman), Bureau of Standards.

This resolution was proposed by Dr. Mees of the American committee,[2] and was seconded by Mr. Bloch of the British committee. It was formulated and adopted after extensive discussion, the details of which may be noted on pp. 171–173 of the Proceedings of the last Congress. It was to a considerable degree a compromise between the more or less conflicting opinions of those interested. It effected the desire expressed in the American committee's reports[3] that the sensitometry of photographic emulsions should be carried out and expressed in terms of a spectral energy distribution approximating that of average noon sunlight, and it incorporated the source-and-filter combination recommended by the committee at the last Congress (Proceedings, p. 153) for producing the desired sunlight quality in the laboratory. The wording of the resolution was such as to meet the desires expressed by Messrs. Guild, Toy, and Smith of England and Prof. Fabry of France (Proceed-

[2] The recommendation just quoted refers twice to the "National Committees" represented at the Congress. It seems certain, however, that the National Standardization Committees, rather than the National Committees, are meant by these two references. The reasons for believing this are as follows:

1. The nations represented at the discussion on pp. 170–173 of the Proceedings of the last Congress are England, France, Germany, and the United States of America. These are the only four nations having National Standardization Committees (see page 566 of The Proceedings); whereas five other nations, in addition to the four just noted, are represented by National Committees (see pp. 564–565 of the Proceedings).

2. The subject under discussion was the report of the American National Standardization Committee, as given on pp. 152–160 of the Proceedings, containing recommendations bearing on the standardization of units and methods for photographic sensitometry.

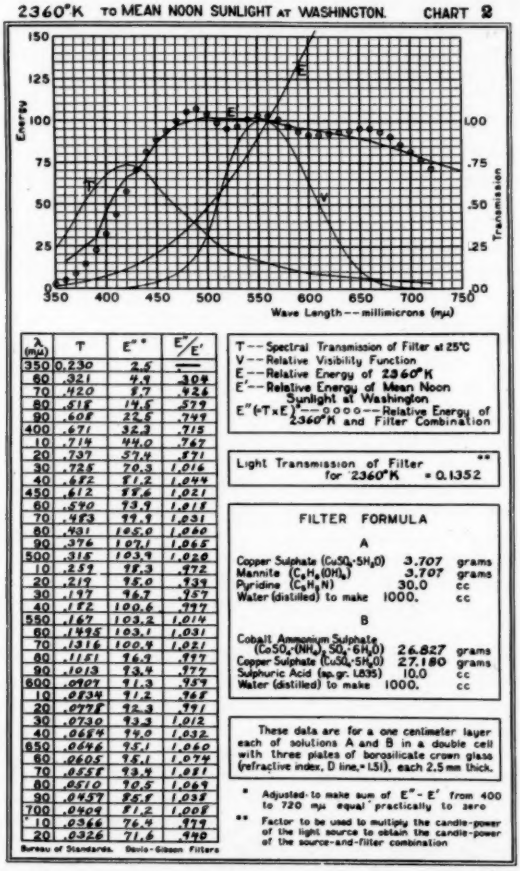
3. The personnel of the French committee, meeting on October 18, 1929 to consider the recommendations of the Seventh International Congress of Photography (the report of the French committee is considered later in the present report) is practically the same as that published for the French National Standardization Committee.

4. Dr. C. E. K. Mees, secretary of the American National Committee and member of the American National Standardization Committee, who was present and took an active part in the discussion preceding the adoption of the recommendation, makes the following statement in this connection (letter of December 10, 1930 to the chairman of the present committee): " . . . in my opinion, the Congress meeting intended by 'National Committees,' the 'National Standardization Committees,' and not the general 'National Committees' properly so-called."

We shall, therefore, assume that the Congress intended the recommendation under consideration to be referred to the four respective National Standardization Committees for approval. In the present report, whenever the respective committees are referred to (e.g., the American committee, the French committee, etc.) it is to be understood that the National Standardization Committees are meant, unless it is otherwise explicitly stated.

[3] Proceedings, Sixth International Congress of Photography, Paris, 1925, pp. 60–70; J.O.S.A. and R.S.I., *12*, pp. 567–586; 1926. Proceedings, Seventh International Congress of Photography, London, 1928, pp. 152–161. A resume of this previous work of the American committee has been recently given by Mr. Loyd A. Jones, former chairman, J.O.S.A., *21*, pp. 361–368; June, 1931.

ings, pp. 171–172) that the spectral distribution be defined by means of a source-and-filter combination realizable in practice rather than in terms of the ideal but strictly unobtainable source recommended by the American committee on p. 152 of the Proceedings of the last Congress.


2360°K TO MEAN NOON SUNLIGHT AT WASHINGTON. CHART 2
Energy
Transmission
Wave Length—millimicrons (mμ)
T—Spectral Transmission of Filter at 25°C
V—Relative Visibility Function
E—Relative Energy of 2360°K
E'—Relative Energy of Mean Noon Sunlight at Washington
E"(=T×E)'—Relative Energy of 2360°K and Filter Combination
Light Transmission of Filter for 2360°K = 0.1352 **
FILTER FORMULA
A
Copper Sulphate (CuSO4·5H2O) 3.707 grams
Mannite (C6H8(OH)6) 3.707 grams
Pyridine (C5H5N) 30.0 cc
Water (distilled) to make 1000. cc
B
Cobalt Ammonium Sulphate (CoSO4·(NH4)2SO4·6H2O) 26.827 grams
Copper Sulphate (CuSO4·5H2O) 27.180 grams
Sulphuric Acid (sp.gr. 1.835) 10.0 cc
Water (distilled) to make 1000. cc
These data are for a one centimeter layer each of solutions A and B in a double cell with three plates of borosilicate crown glass (refractive index, D line, = 1.51), each 2.5 mm thick.
* Adjusted to make sum of E"-E' from 400 to 720 mμ equal practically to zero
** Factor to be used to multiply the candle-power of the light source to obtain the candle-power of the source-and-filter combination
Bureau of Standards. Davis-Gibson Filters

λ (mμ)	T	E"*	E"/E'
350	0.230	2.5	—
60	.321	4.9	.304
70	.420	8.7	.926
80	.518	14.5	.979
90	.608	22.5	.749
400	.671	32.3	.715
10	.714	44.0	.767
20	.737	57.4	.871
30	.725	70.3	1.016
40	.682	81.2	1.044
450	.612	88.6	1.021
60	.540	93.9	1.018
70	.483	99.8	1.031
80	.431	105.0	1.060
90	.376	107.1	1.065
500	.315	103.9	1.020
10	.259	98.3	.972
20	.219	95.0	.939
30	.197	96.7	.957
40	.182	100.6	.997
550	.167	103.2	1.014
60	.1498	103.1	1.031
70	.1316	100.9	1.021
80	.1151	96.9	.977
90	.1013	93.4	.977
600	.0907	91.3	.959
10	.0834	91.2	.968
20	.0778	92.3	.991
30	.0730	93.3	1.012
40	.0684	94.0	1.032
650	.0646	95.1	1.060
60	.0605	95.1	1.074
70	.0558	93.4	1.051
80	.0510	90.5	1.069
90	.0457	85.5	1.038
700	.0409	81.2	1.008
10	.0366	76.4	.979
20	.0326	71.6	.990

FIG. 1. *Chart giving spectrophotometric description of filter recommended by the Seventh International Congress of Photography. This chart is taken from Bureau of Standards Misc. Publ. No. 114.*

By restricting the resolution so as to apply only to the sensitometry of negative material, the objections of Prof. Lehmann and others of Germany were apparently met, these objections referring to the use of the proposed standard in the sensitometry of positive materials.

Questions regarding the suitability of pyridine for filter use were raised by Mr. Guild and by Mr. Calzavara of France and were briefly answered by Dr. Mees (Proceedings, p. 173). The use of pyridine is discussed in detail later in the present report.

In Fig. 1 is given a chart describing the recommended filter. This figure is a reproduction of chart No. 2 from Bureau of Standards, Miscellaneous Publication No. 114.[4]

II. Approval Given by the English and American Committees and the Optical Society of America

The recommendation passed by the Seventh International Congress of Photography, as quoted above, was ratified by the English committee on November 18, 1929. (See memorandum, "Survey of Known Progress Since the Last Congress, 1928," prepared by Dr. Walter Clark, March, 1931.)

The recommendation was also approved by formal vote of the American committee, this vote being in answer to a letter dated December 11, 1929, from Mr. Jones, chairman of the American committee.

Prior to this, the recommendation had been brought to the attention of the Optical Society of America, which organization the American committee represented, and the following resolution was passed by the Council at a meeting on February 23, 1929:

"Moved that the Secretary of the Optical Society be instructed to notify the Secretary of the National Committee of the International Congress of Photography that the Optical Society of America recommends that the American National Committee ratify the recommendation of the Seventh International Congress of Photography (held in London, July, 1928) relating to the international unit of photographic intensity which reads as follows: . . ."

(The recommendation, as quoted above, was hereupon repeated. The draft of the resolution which was at that time available did not, however, contain the word "filtered" given in the fourth line of the resolution as published on p. 173 of the Proceedings; and this fact, together with the presence of the comma after "2360°K" in the sixth line, made the recommendation apparently subject to misinterpretation. The following statements were therefore appended to the resolution.)

"In ratifying this proposal the Optical Society of America understands that the intent of this recommendation is as follows:

"(1) The intention is to specify two things, (a) the *unit* in which the intensities of light sources are to be expressed, and (b) the *quality* of light to be used.

[4] Raymond Davis and K. S. Gibson, *Filters for the Reproduction of Sunlight and Daylight and the Determination of Color Temperature*, Bureau of Standards, Miscellaneous Publication No. 114, pp. 1–165; January, 1931. This paper will be hereinafter referred to as B. S. M. 114.

"(2) The *unit* is to be the International Candle, implying further that the intensities measured and stated will be luminous intensities as in visual photometry.

"(3) The *quality* of light to be used for sensitometry of negative materials is to be that which results from passing the radiation from a grey body at 2360°K normally through the filter described.

"(4) The grey body and the selectively absorbing filter together shall be considered as the effective source in specifying the intensity (candlepower).

"(5) The procedure recommended for determining the intensity of the combined effective source is to multiply the intensity of the primary source (grey body) by the appropriate transmission factor of the filter which is 0.135. This factor has been computed from the spectral transmission of the filter via the relative energy distribution of 2360°K and the relative visibility function adopted by the sixth session of the International Commission on Illumination at Geneva, 1924.

"(6) This resolution does not state or imply the value of illumination to be used at the test plane during the sensitometric exposure, nor does it place any limitations on the intensity of the light source to be used."

To avoid misunderstanding it should be noted that the statements just given are not to be considered as reservations to the vote of approval given by the Optical Society of America. Ratification of the resolution was made without qualification. The statements simply express the American understanding of the sense of the resolution.

III. Regarding the Use of Pyridine in the Recommended Filter

Objections to the use of pyridine in the proposed filter or questions regarding the suitability of using any organic materials for such purpose have been raised as follows:

1. By Mr. Guild, Proceedings of the last Congress, p. 171.

2. By Mr. Calzavara, Proceedings of the last Congress, p. 171; also in an article entitled, "L'Etalon lumineux pour Sensitométrie, Observations sur la composition du filtre coloré," Science et Industries Photographiques, p. 113, Nov., 1928.

3. By the French committee, meeting at the Institut d'Optique, October 18, 1929.

4. By Dr. Luther, in a paper entitled, "Über flüssige Lichtfilter zur Herstellung von künstlichem Sonnenlicht," ZS. f. wiss. Photographie, *29*, pp. 234–238; 1930.

These objections will be considered in turn in the following sections. It is believed they arose in all cases because quantitative information was not available at the time they were made to show how small a change was produced in the spectral transmission of the filter by the impurities and variations of strength to be expected in commercial pyridine. The point was barely touched upon by Davis and Gibson in their

paper, "Artificial Sunlight for Photographic Sensitometry," Proceedings of the last Congress, pp. 161–170. Recently, however, the complete Bureau of Standards paper describing the Davis-Gibson filters has been published.[5] The quantitative spectrophotometric information therein contained will be referred to and used freely in the present report. It is believed the evidence thus exhibited, together with that afforded by Mr. Guild's examination of the pyridine filters (see next section) will remove the distrust with which the use of pyridine has been regarded.

1. GUILD'S CONCLUSIONS REGARDING THE PYRIDINE FILTERS

The International Commission on Illumination has a committee on colorimetry actively engaged in the selection and specification of a "white light" standard for colorimetric purposes. The secretariat of this colorimetry committee is the National Illumination Committee of Great Britain. The extensive series of filters developed by Davis and Gibson include several that are suitable for use with a specified light source to secure a working standard of "white light" for colorimetry. Mr. Guild examined some of the filters, therefore, and came to the following conclusion (p. 10 of memorandum 15 Great Britain 1, National Illumination Committee of Great Britain, Sub-committee on Colorimetry, dated June 13, 1929):

"Several of the Davis-Gibson filters have been made up at the National Physical Laboratory using C.P. pyridine obtained from commerical dealers without taking any precautions about purity. The properties of these filters agreed so closely with those published by Davis and Gibson that we may conclude, so far as Great Britain is concerned, that pyridine can be obtained commercially of sufficient purity to obviate the need for any elaborate precautions."

After further consideration of the matter he made the following statements (pp. 10–11 of memorandum 15 Great Britain 2, National Illumination Committee of Great Britain, Sub-committee on Colorimetry, March 7, 1930:

"The extensive series of filters developed by Messrs. Davis and Gibson have a value which is not measurable by the merits of any one of the filters for any one specific purpose. These filters provide a basis for tackling innumerable problems connected with the colour temperature scale, and with heterochromatic photometry, which is far in advance, as regards completeness and experimental accuracy, of anything hitherto available. There is nothing else comparable with them for such purposes; and research workers on photometry and colorimetry will necessarily use these filters for a variety of purposes, and will become familiar with the technique of their construction and use. There is no corresponding compendium of information available as regards the equivalent series using ammoniated copper sulphate, in which we at present know only the properties of the two filters specifically designed for the N.P.L. standard. For this reason, after carefully weighing all the issues involved, I am of opinion that the committee ought to recommend a new standard employing filters from the Davis-Gibson series."

[5] B. S. M. 114. (See reference above.)

The objections that were raised by Guild at the last Congress (Proceedings, p. 171) have apparently, therefore, been satisfactorily met by his own tests. His conclusions regarding the spectrophotometric reproducibility of the pyridine filters are in complete agreement with the evidence in this respect published by Davis and Gibson and considered later in this report. His reasons for recommending that the pyridine filters be used for colorimetric work instead of the ammonia filters (which were developed under his supervision and with which he is personally wholly satisfied) apply with equal force in the case of photographic sensitometry. *The American committee feels that these statements of Guild's are of great importance and earnestly urges their careful consideration by those who have believed pyridine unsuitable for filter use.*

2. CALZAVARA'S OBJECTIONS TO THE USE OF PYRIDINE

A considerable part of Mr. Calzavara's objections to pyridine are based on the difficulty of making *synthetic* pyridine. However, it is very improbable that any synthetic pyridine ever appears on the market. Commerical pyridine is at present obtained almost exclusively from coal tar. The low boiling constituents of coal tar (benzene and its homologues) are extracted with sulphuric acid to remove basic materials, and the bases are later recovered by neutralizing the sulphuric acid and distilling. The "C.P." product[6] is obtained probably merely by fractional distillation of the crude product. The cost of synthetic pyridine would be enormously higher than that of the coal tar material, and the crude product of any of the synthetic reactions is probably more difficult to purify than the coal tar crude.

The standard spectrophotometric data published by Davis and Gibson were obtained with solutions prepared with commercial pyridine. All the 17 samples of pyridine examined by them were samples of commercial pyridine, and they have published no data at all except as obtained with commercial pyridine. Objections to the proposed filter based on the difficulties of preparation of pure synthetic pyridine have, therefore, no weight.

A second objection raised refers to the difficulty of obtaining pyridine completely free of water. This difficulty arises in the preparation of commercial pyridine as well as of synthetic pyridine, but is of no practical importance in the preparation and use of the pyridine solution. It is,

[6] The term "C.P.", originally intended to indicate a chemically pure product, is now a trade designation of somewhat variable meaning in the American chemical industry. As applied to pyridine in this report, it is the manufacturers' designation of the best grade obtainable on the open market.

of course, wholly unnecessary to secure completely anhydrous pyridine for the purpose of preparing aqueous solutions. At the most a knowledge of the water content is sufficient to insure the necessary precision of pyridine concentration. However, commercial pyridine of the C. P. grade has been found to be sufficiently anhydrous for use without analysis. The pyridine used by Davis and Gibson in obtaining their fundamental spectrophotometric data analysed 98.4 percent by acid titration, complete analysis showing 96.4 percent pyridine, 2.4 percent α-picoline, and 1.2 percent water. Of all the 17 samples of commercial pyridine examined, none deviated in strength from the standard of 98.4 percent by more than ± 1.6 percent. The effect of such variation on the spectral transmission of the filter is shown later in this report to be *wholly unimportant*—less than the effect of variations of copper content in the copper sulphate, or the effect caused by a change of thickness corresponding to the tolerance given on page 173 of the Proceedings of the last Congress.

In brief: (1) It is unnecessary to use completely anhydrous pyridine in preparing the proposed filter; (2) The "Editor's Note" on page 173 of the Proceedings is in error; (3) The pyridine used in deriving the specified spectrophotometric data for the filter was not completely anhydrous but titrated 98.4 percent strength as stated by Davis and Gibson on p. 169 of their paper published in the Proceedings of the last Congress; (4) The strength of commercial pyridine of the C. P. grade will not deviate to any important extent from that used as standard, as shown by the work of Guild (above) and of Davis and Gibson (below).

The third class of objection stated by Calzavara has reference to the presence of impurities (other than water) in pyridine. From the nature of the source, the principal impurities of crude coal-tar pyridine may be expected to be other cyclic nitrogen bases. The methyl pyridines (picolines) are the most difficult to remove by distillation and are therefore the commonest impurities. The list of possible impurities cited by Calzavara represents simply the classes of compounds which do not react with Grignard reagents, regardless of the probability of their occurrence. It is probable that the only appreciable impurities in C. P. pyridine are water and homologues. The most important of these homologues is α-picoline.

The effect of this impurity on the spectral transmission of the filter was studied by Davis and Gibson and is noted below. Their work and the measurements of Guild, noted above, show that, if yellowish pyridine be avoided, the effect of any impurities on the spectral transmission

of the filter is negligible, provided solution A be prepared from pyridine of C. P. quality.

Calzavara's objections to the use of pyridine do not, therefore, afford any basis for rejection of the proposed filter as a standard for photographic sensitometry. The fact that pure synthetic pyridine is difficult to prepare is of no weight because commercial pyridine, readily available in England and America, and presumably also in France, Germany, and elsewhere, is not prepared that way. The fact that it is difficult to prepare pyridine completely anhydrous is of no weight because that used in the spectrophotometric standardization of the filter was not completely anhydrous and the variations in strength found in commercial pyridine of the C. P. grade exert a wholly negligible effect on the spectral transmission of the filter. The fact that a large number of possible impurities might conceivably be present in pyridine is completely outweighed by the evidence showing that the use of commercial pyridine results in a filter whose reproducibility is wholly satisfactory from the spectrophotometric standpoint. In fact, Calzavara's objections might in turn be criticized because of the complete lack of spectrophotometric evidence given by him in support of such objections. *No criticism of the use of pyridine is valid unless the point raised can be shown to have an important effect on the spectral transmission of the filter.*

3. MEETING OF FRENCH NATIONAL STANDARDIZATION COMMITTEE

A meeting of this committee was held on October 18, 1929, at the Institut d'Optique under the presidency of Mr. Fabry. An English translation of the report of this meeting was forwarded to the chairman of the American committee by Dr. Slater Price.

Reference was therein made to the two ammonia filters developed at the National Physical Laboratory, and the French committee apparently favored the use of ammonia to pyridine. However, the only specific objection to the use of pyridine was stated as follows:

> "MM. Jouaust and Calzavara viewed with regret the adoption of a filter involving the use of organic substances; this filter would be employed especially by physicists who would, in general, have no facility for controlling the purity of their stock materials."

This objection to the use of pyridine is answered elsewhere in detail in the present report (sections III-2 and III-5). It may be merely noted here that spectrophotometric tests have shown that it is no more necessary to test for the strength and purity of pyridine than for the strength and purity of copper sulphate, and that such slight variations as may be expected to occur are of negligible importance.

As a result of this meeting the French committee planned a comparative study of the proposed filter containing pyridine and a similar one containing ammonia. The complete paper describing the pyridine filters (B.S.M. 114), and the conclusions of Guild (section III-1 of the present report), were not available to the French committee at the time their decision was made. With such evidence now available, further comparison between pyridine and ammonia filters would appear unnecessary. Other questions discussed by the French committee are considered in the present report in the sections devoted to those subjects.

4. LUTHER'S PROPOSAL OF A COPPER-GLYCOCOLL SOLUTION

In the paper referred to above, Dr. Luther describes the preparation of the copper salt of glycocoll, $Cu(NH_2 \cdot CH_2 \cdot COO)_2 + H_2O$, molecular weight 229.7. Compared with the pyridine-mannite solution of copper sulphate, the copper-glycocoll solution is said to show less absorption in the ultraviolet, "was nur ein Vorteil ist," while in the visible the absorption curves are very generally similar, differing only in that the copper-glycocoll curve is displaced 8–10 mμ towards the red. The author further states that this difference may be compensated by reducing the concentration of copper sulphate in solution B and believes that a better approximation can be obtained with copper glycocoll than with the pyridine-mannite solution of copper sulphate. No quantitative data are given, however, to support this last statement.

Messrs. Davis and Gibson have prepared solutions of copper glycocoll of appropriate concentrations, have determined their spectral transmittancies and have derived the energy distribution obtainable with a 2360°K source when the copper-glycocoll solution is combined with the copper and cobalt components of solution B—all by methods similar to those used in designing the filters of B.S.M. 114. The results are shown in Fig. 2. The ideal energy distribution chosen for duplication is the mean noon sunlight distribution used as the ideal in the development of the filter recommended by the last Congress and shown in Fig. 1 of the present report. It will be noticed that the duplication of the sunlight energy distribution is distinctly inferior in the case of the glycocoll filter, Fig. 2, to that shown by the pyridine filter, Fig. 1. This inferiority is directly traceable to the displacement of the copper-glycocoll transmittancy curve towards the red relative to the copper-pyridine curve. This displacement results in excess transmission in the yellow-green region, which in turn results in the notable excess of transmitted energy shown in this region by the two copper-glycocoll energy distribution curves of

Fig. 2. The copper-glycocoll absorption band is apparently fixed in position with respect to wave length, the only change being to increase or decrease the absorption as the copper concentration is varied. It, therefore, seems impossible to improve the energy-distribution match over that shown in Fig. 2.

With pyridine, on the other hand, it is possible to vary the wave length of maximum absorption over a considerable range by varying the amount of pyridine, as is illustrated later in Figs. 4 and 5. The best energy-distribution match with the ideal will be obtained when the

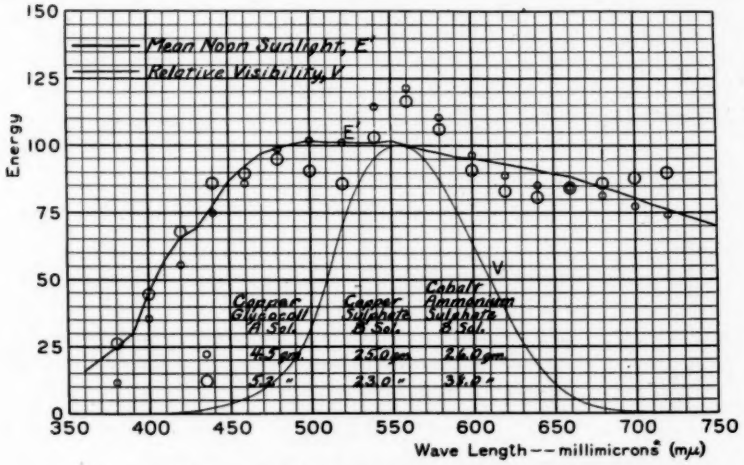


FIG. 2. *Energy distribution obtainable with filter using copper glycocoll as basis for solution A. Compare with energy distribution obtainable with pyridine as shown in Fig. 1.*

maximum absorption of the copper-pyridine solution is properly allocated, with respect to wave length, between the absorption bands of the cobalt and copper salts of solution B. In the design of the filter recommended by the last Congress, Davis and Gibson chose a concentration of pyridine, 30 cc per liter, such as to give the closest possible match with the ideal energy distribution. The results of this study are described in Sec. VII-3 of B.S.M. 114. Fig. 31 of that paper is reproduced herein as Fig. 3, in which is shown the marked superiority resulting from the use of 30 cc of pyridine over that resulting from 10 cc or 100 cc. It may be noted that 10 cc of pyridine gives the same excess transmission in the yellow-green as does the copper-glycocoll solution.

The use of copper glycocoll would, therefore, be a step backward in the development of an accurate sunlight filter unless such a solution

possesses other properties notably superior to those of the pyridine filter. Luther considers the stability of the copper-glycocoll solution superior to that of both the pyridine-mannite and the ammonia solutions of copper sulphate, his conclusions being derived from tests of the three solutions at high temperatures in sealed tubes. However, since the pyridine-mannite solution shows practically no change in transmittancy for a month or two after preparation and very little change during the first year after preparation, its stability is wholly satisfactory for the purpose. The slight change that takes place with time is described in detail

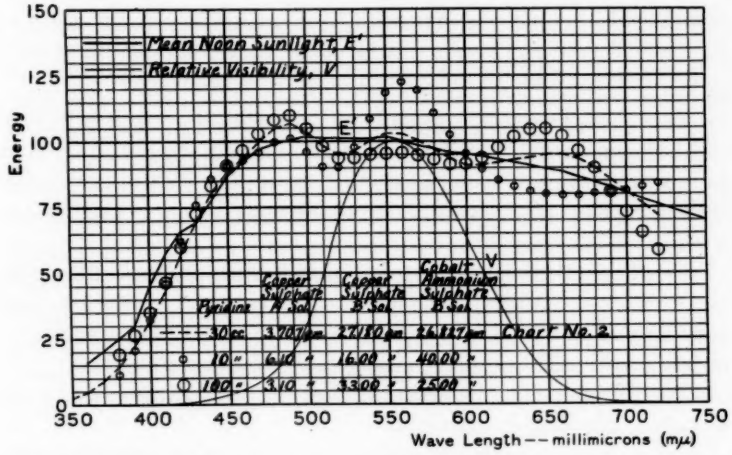


FIG. 3. *Effect on final energy distribution caused by using varying amounts of pyridine. Note the marked superiority in the energy-distribution match obtainable with 30 cc of pyridine as compared with 10 cc or 100 cc. This illustration is taken from Bureau of Standards Misc. Publ. No. 114.*

in B.S.M. 114, Secs. VII-3 and VIII-2-(e). It may be noted that Luther speaks of increased absorption in the violet and ultraviolet with age ("Die erhöhte Extinction im Violett und U.V. bei älteren Lösungen ist auf Oxydation durch Luftsauerstoff zu schieben"), whereas the data in B.S.M. 114 show slightly decreased absorption in this region after a year's time.

Luther states that a copper-glycocoll solution has the following advantages over the pyridine-mannite and ammonia solutions of copper sulphate:

1. The absorbing material may readily be prepared in chemically pure form and may be weighed with sufficient accuracy. The safeguarding materials mentioned need not be accurately weighed.

2. The solution contains no volatile and no easily oxidized materials.
3. The solution is neutral, therefore, does not attack the glass walls of the cell.
4. The solution keeps practically indefinitely.
5. The absorption is only slightly dependent on the temperature.

He states that it has the following disadvantages:

1. The solution can mold (Preservative: Thymol)
2. The solution is sensitive to alkali and acid. This sensitivity can be largely reduced by suitable additions.
3. The solubility of the copper salt of glycocoll is not very large at room temperature.

So far as the so-called advantages are concerned, however, it would seem that the pyridine solution is fully as satisfactory as the glycocoll solution. The following points may be noted, the paragraphs being numbered to correspond with the "advantages" listed above:

1. It is shown elsewhere, both in the present report and in B.S.M. 114, that commercial pyridine may readily be obtained of a strength and purity wholly satisfactory for the purpose. The statements regarding the weighings apply equally well to the components of the pyridine filter.

2. Pyridine is less volatile than water itself. The tendency of the pyridine solution to oxidize is balanced by the tendency of the glycocoll solution to mold. Such slight change as takes place in the former is accurately known and has been considered above under stability.

3. The pyridine-mannite solution does not attack the glass of the cells to any appreciable extent.

4, and 5. These statements apply equally well to the pyridine solution. Such changes as do occur are accurately known.

In conclusion, therefore, the American committee believes the following statements to be correct:

1. A filter containing a solution of copper glycocoll possesses no distinct advantage over the recommended filter containing pyridine and mannite.

2. The energy distribution obtainable with the glycocoll solution is a less accurate reproduction of noon sunlight than that obtainable with the recommended filter.

3. The reasons given by Guild (see quotation in section III-1) for recommending the use of pyridine filters in preference to ammonia filters apply equally well to the use of pyridine in preference to glycocoll.

Before concluding the discussion of Luther's paper it may be noted that he discusses methods for insuring that the copper and cobalt salts contain their proper nominal content of water of crystallization. Such

information is of interest, but in view of the evidence presented elsewhere in this report, it seems to be an unnecessary refinement so far as copper sulphate and cobalt ammonium sulphate are concerned. It would undoubtedly assist in securing a more accurate reproduction of the filter if the latter salt is not available and cobalt sulphate has to be used.

5. REPRODUCIBILITY OF PYRIDINE

It may be repeated that the variations in the strength of pyridine caused by incomplete dehydration, and the presence of impurities in pyridine—in other words, the fact that pyridine is an organic material difficult to obtain in a condition of 100 percent strength and purity—*are of no importance whatsoever except as they affect the spectral transmission of the filter*. The reproducibility of the pyridine chemically is not of primary importance. *The important things* are (1) whether or not the spectral transmission of the solution or filter is reproducible when the pyridine is combined with the other materials in the proportions specified, and (2) the magnitudes of the deviations in spectral transmission to be expected from variations in the strength and purity of commercial pyridine of the C.P. grade as compared to (a) the magnitudes of the similar deviations to be expected from variations in the strength and purity of the other materials used in the filter and (b) the tolerances for thickness of solution and weights of salts as stated at the bottom of page 173 of the Proceedings of the last Congress.

(a) *As to Strength*

The nature and magnitude of the change that takes place in solution *A* when the amount of pyridine is varied are illustrated in Figs. 24 and 8 of B.S.M. 114, which are reproduced in the present report as Figs. 4 and 5. From these data the change in spectral transmission that occurs when the strength of pyridine deviates from normal may be accurately computed.

In cooperation with the Eastman Kodak Company, Davis and Gibson examined 17 different samples of commercial pyridine. The strengths of these 17 samples, as determined by titration tests, varied from 97.0 to 100.0 percent. The strength of the pyridine used by Davis and Gibson in deriving their standard spectrophotometric data on the filters was 98.4 percent, as stated by them on p. 165 of the Proceedings of the last Congress. Out of the 17 samples examined, therefore, none of them deviated in strength from the standard used by Davis and Gibson by more than about 1.5 percent.

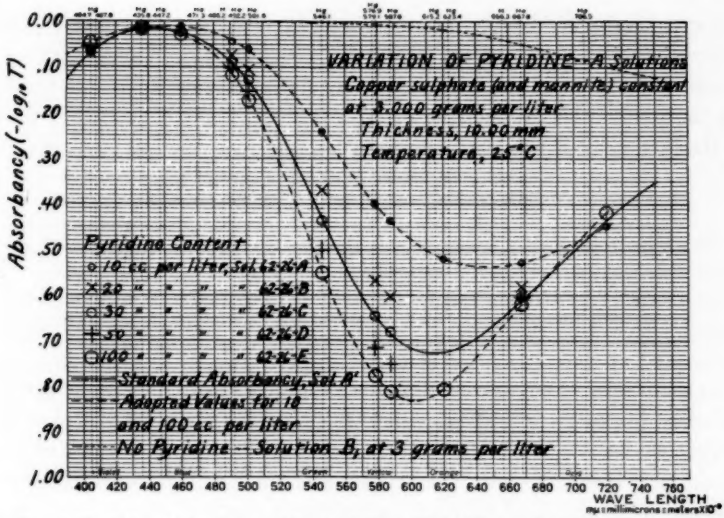


FIG. 4. *Variation of absorbancy of the A solution with pyridine content. These data are plotted as a function of pyridine content in Fig. 5. This illustration is taken from Bureau of Standards Misc. Publ. No. 114.*

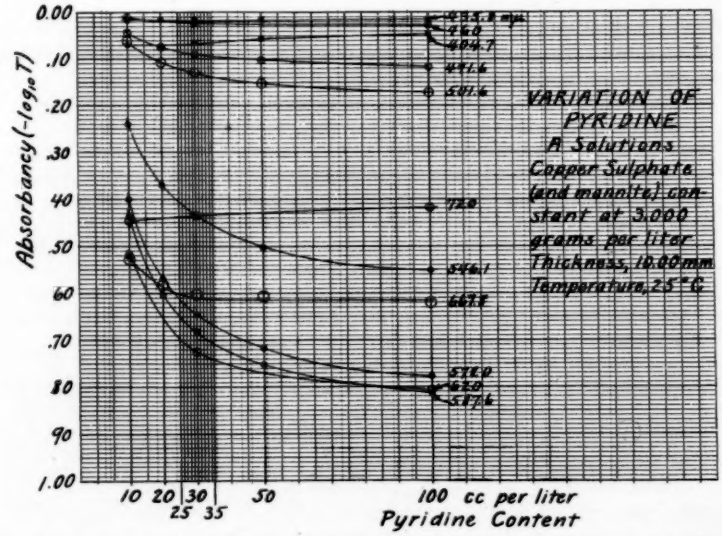


FIG. 5. *Variation of absorbancy of the A solution with pyridine content. These data are plotted as a function of wave length in Fig. 4. This illustration is taken from Bureau of Standards Misc. Publ. No. 114.*

From Figs. 4 and 5 it may be noted that the maximum percentage change in the spectral transmission of solution *A* with change of pyridine occurs at approximately 587.6 mμ. Computation at this wave length shows that, for the 3.707-gram solution used in the proposed filter, a variation of 1.5 percent in the pyridine strength will produce a variation of only 0.7 percent in the transmission of the filter, and this is the maximum change that occurs at any wave length.[7] Obviously such a small change is wholly negligible; in fact, a deviation several times as large would be of no importance in photographic sensitometry.

It is next of interest to see how the deviations to be expected from the variations in the strength of commercial pyridine compare with the deviations caused by variations from the theoretical copper content of the same solution or by variations in weight of copper sulphate or thickness of cell equivalent to the tolerances stated.

The effect of change or error in the pyridine strength is somewhat similar to that caused by change or error in the copper strength of the *A* solution. If the copper content is varied, the maximum change will occur at the wave length of maximum absorbancy, approximately at 613 mμ. At 610 mμ a variation of 0.4 percent in the copper content of solution *A* produces 0.7 percent change in the spectral transmission of the filter.[8]

It so happens that the tolerance in weighing specified ("For practical purposes an accuracy to the second place of decimals is probably sufficient," Proceedings, last Congress, p. 173) is of this order of magnitude. If an error of 0.01 gram be allowed, there results 0.01/3.707 or 0.27 percent error in the copper content. Furthermore, of course, unless special precautions are taken, the strength of copper sulphate crystals will vary by this amount (and even more, up to ±1 percent) due to fluctuations in the water content of the crystals.

[7] This value is derived as follows: 1.5 percent variation in pyridine strength or content is equivalent to a variation of 0.45 cc (0.015×30=0.45) of pyridine. The difference in absorbancy corresponding to a change of 10 cc of pyridine (i.e., 25 cc to 35 cc) is 0.708−0.650=0.058. Therefore, the difference corresponding to 0.45 cc equals 0.058×0.045=0.0026. This, however, refers to a 3-gram solution. For the 3.707-gram solution, the difference would be 0.0026×3.707/3.000=0.0032. Absorbancy is the negative logarithm (to base 10) of the transmittancy and a change in absorbancy of 0.00434 is equivalent to a change of 1 percent of the transmittancy. 0.0032/0.00434=0.74.

[8] This value is derived as follows: The absorbancy of the 3.707-gram solution at 610 mμ is 0.891. Therefore, 1 percent change in copper content will cause a change in absorbancy of 0.00891. Since a change in absorbancy of 0.00434 is equivalent to 1 percent change in transmittancy, it requires 0.49 percent change in copper to cause 1 percent change in transmittancy, and 0.36 percent change in copper to cause 0.74 percent change in transmittancy.

The tolerance in thickness stated on page 173 of the Proceedings of the last Congress was "± 0.05 mm," this applying to both the *A* and *B* solutions. The absorption bands produced by the cobalt of solution *B*, by solution *A*, and by the copper of solution *B*, have maxima occurring near 510, 610, and beyond 720 mμ, respectively. At these three wave lengths a variation of 1/2 percent in the thickness of both the solutions produces the following changes in the transmission of the filter:

Wave length in millimicrons	Percentage change in transmission
510	0.6
610	1.2
720	1.6

Variation of thickness within the tolerance allowed by the last Congress, therefore, produces a maximum effect about twice as great as that to be expected from variations in the strength of commercial pyridine.

It may, therefore, be concluded with reference to the filter proposed for sensitometric use at the Seventh International Congress of Photography:

1. *The errors or deviations in spectral transmission caused by variations to be expected in the strength of commercial pyridine of the C P grade are negligible. They are apparently even smaller and of less importance than those caused by variations to be expected in the copper content of the copper sulphate used in the same solution. They are likewise somewhat less than those produced by variations in thickness of the solutions within the tolerance specified at the last Congress, and are of the same order of magnitude as those caused by weighing within the tolerance likewise specified.*

2. *There is no more need for testing or stating the strength of the pyridine used than there is for testing or stating the copper content of the copper sulphate used.*

(b) *As to Purity*

It has already been pointed out that the impurity most likely to be present in pyridine (aside from a small amount of water) is the homologue *α-picoline*. The spectral trasmission of α-picoline was studied by Davis and Gibson, both as an impurity of known amount in solution *A* and also with copper sulphate in aqueous solution without pyridine. The results are shown in Fig. 6, which is a reproduction of Fig. 27 of B.S.M. 114.

It may be noted that the most important effect of the α-picoline impurity is in the violet. Based on the absorbancy values at 404.7 mμ (Fig. 6), it was estimated that the pyridine used in deriving the standard spectrophotometric data for the Davis-Gibson filters contained about 2.5 percent of α-picoline and this was checked by chemical analysis. Since none of the 17 samples of commercial pyridine examined contained as much as 5 percent α-picoline, it is apparent that the pyridine used by Davis and Gibson well represents the average of what may be expected in commercial pyridine of the C.P. grade as regards its commonest and most important impurity.

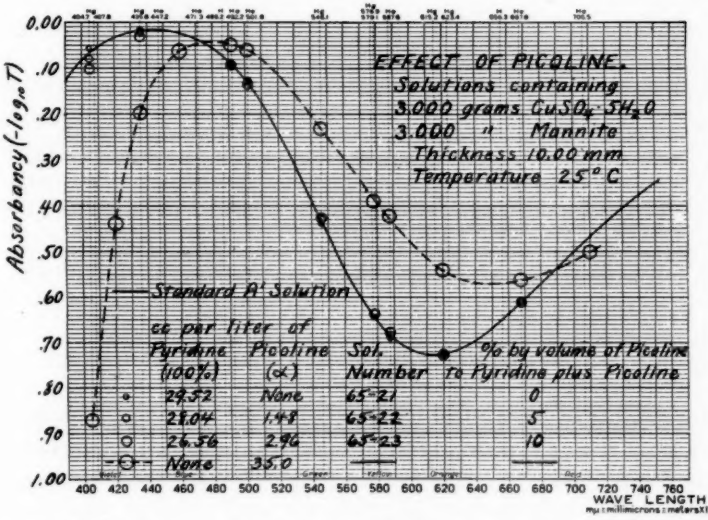


FIG. 6. *Effect of α-picoline on the absorbancy of the standard A' solution. α-Picoline is one of the next higher homologues of pyridine and may be present in small amounts as an impurity in the pyridine. The pyridine used in obtaining the standard data of this paper contained 2 1/2 percent of α-picoline. This illustration is taken from Bureau of Standards Misc. Publ. No. 114.*

The maximum deviation from the standard spectrophotometric data caused by the presence of α-picoline in the pyridine in amounts from 0 to 5 percent is approximately one percent of the transmission except in the violet (and perhaps the ultraviolet). At 404.7 mμ such deviations amount to about 3 percent of the transmission for a 3.707-gram solution.

There seem to be no other impurities in pyridine which affect the spectral transmission of the filter to an appreciable amount. Two other

things may be noted, however, which if avoided will definitely improve the spectrophotometric reproducibility of the filter. The first precaution to note is that *distinctly yellow pyridine should not be used*. The effect on the filter is slight, due to the fact that the pyridine in the filter is diluted to 30 cc per liter, and amounts to but a few percent in the violet (see B.S.M. 114, p. 113 and Fig. 28). However, since the colorless pyridine is so readily available, the use of yellow pyridine should be avoided.

The second precaution to take is *not to filter the A solution through paper*. To do so may weaken the copper concentration of the solution, as a reaction will take place between the filter paper and the solution with a slight loss of copper.

It should be noted, however, that while the use of yellow pyridine and the filtering of the *A* solution are undesirable and unnecessary, even the lack of such precautions would not invalidate the use of the filter for photographic sensitometry. This was shown in the report of the American committee at the last Congress(Proceedings, p. 159). The filters there referred to contained *A* solutions that had been filtered, one of which furthermore had been prepared with yellowish pyridine. *For sensitometric purposes these particular filters were found to be practically identical*. Further information concerning them is given in B.S.M. 114, pp. 102–110.

IV. Regarding the Use of Mannite in the Recommended Filter

Mannite (d-mannitol) may be obtained either as a natural product, which is the common source, or by reduction of the common and readily purified sugar, fructose. It is readily purified by crystallization. The spectral transmission of solution *A* is the same whether mannite is present or not. Its presence, however, is necessary to prevent a slow precipitation of copper hydroxide from the faintly alkaline solution.

The only specific criticism of the use of mannite is made by Calzavara in the article noted above. The substance of this criticism seems to be based on the variability of its rotatory power in the presence of other materials.

If the recommended filter, containing mannite, produced a measurable rotation of the plane of polarization, such need cause no trouble in use, any more than does an absorption cell with crystalline quartz end plates, since the spectral distribution of energy ordinarily obtained with the filter would not be modified unless it were placed between two nicol prisms (or in an equivalent position) and this need never be done.

However, the test described in B.S.M. 114, pp. 37–38, shows that *the filter possesses no measurable rotatory power.*

General criticism of the use of mannite is made in the report of the meeting of the French committee noted above, in which it is stated: ". . . the members of the Committee were unanimous in considering that the use of solutions containing pyridine and mannite might, in practice, present difficulties. . . ." Here, as in Calzavara's article, however, no spectrophotometric evidence is given to warrant such fear. The mere fact that a substance is an "organic material" is hardly sufficient to condemn it, a priori, for filter use.

In view of the positive evidence given elsewhere in this report regarding the reproducibility of the filter, and in view of the fact that the mannite produces no measurable rotation of the plane of polarization and has no effect on the spectral transmission of the filter except to produce stability, it would seem that there are no valid grounds for objections to its use.

V. REGARDING THE USE OF COBALT AMMONIUM SULPHATE IN THE RECOMMENDED FILTER

The use of cobalt ammonium sulphate, $CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, has been criticized[9] on the ground that no European manufacturer of pure chemicals was in a position to supply crystallized cobalt ammonium sulphate. The objection was answered by Eder,[10] who pointed out that the cobalt ammonium sulphate could be effectively duplicated for filter use by simply combining cobalt sulphate and ammonium sulphate in the proper proportions. Luther (loc. cit.) calls attention to the fact that cobalt ammonium sulphate, crystallizing with six molecules of water, can readily be prepared by mixing concentrated solutions of the components (with ammonium sulphate in slight excess), the salt then being recrystallized from hot water.

However, cobalt sulphate may be used, if desired, without ammonium sulphate. It is pointed out in B.S.M. 114 (pp. 85–86, 98–102) that in the thicknesses and concentrations used in the filters there is no certain difference (such difference, if any, is less than 1 percent) in the spectral transmission of solution *B* (mixture of copper and cobalt salts) whether cobalt sulphate or cobalt ammonium sulphate be used, pro-

[9] Sci. et Ind. Phot. *9A*, p. 10; Jan., 1929. See, also, Kinotechnik, *11*, p. 52; Jan., 1929.

[10] Lichtstandard für Sensitometrie und das Davis-Gibsonsche Lichtfilter mit Kupfer-Kobalt-Lösungen, J. M. Eder, Zs. f. wiss. Phot., *26*, pp. 373–374; 1928–29. See, also, Kinotechnik, *11*, p. 90; Feb., 1929.

vided only that the same amount of cobalt be used in the respective cases. Cobalt ammonium sulphate is specified because it is a much more stable compound with respect to its water of crystallization than is cobalt sulphate. However, if means be available for testing the strength of cobalt sulphate, either chemically or spectrophotometrically, it is entirely suitable for use in the filter. In fact, for photographic sensitometry cobalt sulphate can probably be used safely without analysis.

Here, as elsewhere, the effect on the spectral transmission should be considered. The maximum absorption of cobalt sulphate or cobalt ammonium sulphate is in the green at 513 mμ, approximately. At this wave length the absorbancy of solution *B* in the recommended filter, resulting from the cobalt alone, is 0.324. It therefore requires 1.3 percent change or error in cobalt content ($0.00434/0.00324 = 1.34$) to cause 1 percent change or error in transmission at the wave length of maximum absorbancy, and it would require approximately 2 percent variation in the cobalt content to produce a change in the transmission (at 513 mμ) as great as is produced (at 610 mμ) by a variation of 0.05 mm in the thickness of the *A* solution.

Lack of cobalt ammonium sulphate need not, therefore, prevent the preparation and use of the filter for photographic sensitometry, inasmuch as cobalt sulphate may be used in its stead, either with or without ammonium sulphate, provided that the cobalt (Co) *content be kept unchanged.* While cobalt ammonium sulphate is to be preferred because of its greater stability of water content, the use of cobalt sulphate would seem entirely feasible for sensitometric measurements. Only in case the transmission in the green must be known accurately would it be necessary to test the strength of the cobalt sulphate. No tests of strength need be made if cobalt ammonium sulphate is used.

The following comments regarding the purity of the cobalt salt are taken from the report of the French committee already noted:

"M. Calzavara added that the purity of the cobalt salt ought to be controlled by spectroscopic methods. The purest sample of cobalt sulphate that he had been able to obtain contained quite appreciable traces of nickel salt. M. Sanfourche, chemist at the laboratories of Cie de St. Jobain, had kindly offered to test the purity; after fractionating, the yield of cobalt sulphate quite free from nickel was only 10 percent. M. Fabry supposed that a product a little less pure (the maximum allowable content of nickel salts would have to be fixed) would not introduce appreciable error."

The cobalt salt used by Davis and Gibson in determining the spectrophotometric data on which the design of the filter is based contained a ratio of nickel to cobalt (Ni:Co) of 1:200. It is shown by them (B.S.M.

114, pp. 112–113) that *a nickel content varying from zero to* 1:100 *will change the spectral transmission of the filter from that specified by not more than* 1/4 *percent.* This maximum effect occurs in the violet. It is obviously wholly negligible, in agreement with Fabry's expectations, and unless the cobalt salt is grossly contaminated with nickel no concern need be felt regarding its effect on the transmission of the filter. "Technical" cobalt salts are liable to such gross contamination, but samples of the CP grade obtained from three American manufacturers all had a nickel: cobalt ratio not greater than 1:100.

VI. RECOMMENDATIONS TO THE EIGHTH INTERNATIONAL CONGRESS OF PHOTOGRAPHY[11]

The American committee strongly urges the adoption of the recommendation passed by the Seventh International Congress of Photography, as given on the lower half of page 173 of the official Proceedings of that Congress and as quoted in Section I of the present report—excluding, however, the "Editor's note" (Proceedings, p. 173) which is in error and which was not a part of the official recommendation. To effect the adoption of this recommendation, in compliance with the last sentence therein, it must be approved by the other two National Standardization Committees as has already been done by the English and American committees. It is earnestly hoped that this will be done prior to the meetings of the Eighth Congress, now that the information contained in the present report is available to these committees, in addition to the complete Bureau of Standards publication (B.S.M. 114, complete reference above, Sec. I) describing the large number of filters, including the one specified, designed for use in photographic sensitometry, colorimetry, and photometry.

The American committee affirms that its understanding of the intent of the recommendation is in accord with that stated by the Optical Society of America in its vote of ratification, as quoted in Section II of the present report.

The American committee further recommends:

1. That if cobalt ammonium sulphate ($CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) be not available, the use of cobalt sulphate (nominally $CoSO_4\ 7H_2O$), either with or without ammonium sulphate, be not considered a violation of the specification. The proper amount of cobalt sulphate to use is 19.08 grams per liter.

2. That if borosilicate crown glass of 2.5 mm thickness be not avail-

[11] Held in Dresden in August, 1931.

able, it shall not be considered a violation of the specification (for the purposes of photographic sensitometry) if borosilicate crown glass of not to exceed 4 mm, or if any practically colorless (when viewed edgewise) plate glass of not to exceed 4 mm, be used in lieu of that specified.

The American committee would also call attention to the fact that the action of the last congress (p. 172 of the Proceedings) with reference to the second and third recommendations of the previous American committee was apparently rescinded (p. 173), and no further action with reference to these two reccommendations was taken. The present Committee recommends that Mr. Renwick's proposed resolution (p. 172) be adopted, which reads as follows:

"In all publications which mention the use of a photographic unit of intensity, the illumination received by the sensitive layer shall be specified."

The present committee believes that no further recommendations are necessary at this time in this connection, since Mr. Renwick's resolution replaced the second American recommendation, and since the third American recommendation was essentially adopted at the Sixth International Congress at Paris, in 1925.

ULTRAVIOLET AND LIGHT REFLECTING PROPERTIES OF ALUMINUM

By A. H. Taylor and Junius D. Edwards
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Received July 24, 1931]

Introduction

The recent development of new artificial sources of ultraviolet radiation which are also good light-sources has made possible an era of dual-purpose lighting,[1] combining light for vision and ultraviolet radiation for health maintenance. However, the efficient utilization of ultraviolet radiation requires new methods of fixture design, since many materials which transmit or reflect light efficiently absorb a large portion of the biologically-effective ultraviolet.

Aluminum, properly prepared, apparently reflects ultraviolet radiation more efficiently than any other metal. This is quite fortunate since it is a very convenient metal for use in lighting fixtures and the methods of treating the reflecting surface are not especially complex. The investigation undertaken by the authors had for its purpose the determination of one or more good methods for preparing aluminum surfaces for efficient light and ultraviolet reflection, and the measurement of the reflection characteristics of the surfaces produced. The specimens were prepared in the Aluminum Research Laboratories, Aluminum Company of America, New Kensington, Pa., and all reflection measurements were made in Lighting Research Laboratory, General Electric Company, Nela Park, Cleveland, Ohio.

Etching Aluminum for Reflectors

Etching aluminum to obtain a bright, socalled "frosted finish," has long been a commercial practice.[2] The customary procedure is to treat the aluminum article with a hot solution of sodium hydroxide (caustic soda) followed by treatment with strong nitric acid. This treatment generally increases the reflectivity of the aluminum for both visible and ultraviolet light. However, when maximum reflectivity is desired, other etching treatments have been developed which give superior results. Etching with hydrofluoric and nitric acid has been found to be particularly effective in this respect, as is also etching with a mixture of sodium hydroxide and sodium fluoride followed by nitric acid. The details of these etching treatments are as follows:

ETCH WITH HYDROFLUORIC ACID

The hydrofluoric acid is prepared by adding one volume of concentrated hydrofluoric acid (48% HF) to 19 volumes of water. The nitric acid solution is made by adding one volume of concentrated nitric acid to one volume of water. The etching treatment is as follows: The aluminum article is dipped in the hydrofluoric acid solution, which is held at a temperature of 50 to 60 degrees Centigrade. It is held in this solution for a length of time sufficient to produce the desired etch. It is then removed, washed in warm water, and immersed in the nitric acid solution for a period of about 30 to 40 seconds. The nitric acid solution is kept at room temperature, and immersion in this solution is for the purpose of removing any dark colored film remaining from the first treatment. It is then removed, washed in water, and if there is still any film adherent it is removed by wiping with a wet cotton cloth.

In carrying out this treatment, the hydrofluoric and nitric acids might be used in the same concentrations as described above but mixed in a single solution; it is not usually economical to do so, however, since the hydrofluoric acid is exhausted faster than the nitric acid.

ETCH WITH SODIUM HYDROXIDE-SODIUM FLUORIDE

In this etching treatment the aluminum article is immersed in a solution containing 5 percent sodium hydroxide plus 4 percent sodium fluoride plus 91 percent water. This solution is used at a temperature of 90 degrees Centigrade and the article immersed for a sufficient length of time to produce the desired etch. It is then removed, washed, dipped in the nitric acid solution (1 part water to 1 part acid), then removed and washed as in the previous etching treatment.

ETCH WITH SODIUM HYDROXIDE-SODIUM CHLORIDE:HYDROFLUORIC ACID

Two of the samples later described (ANF and DNF) were given a combination etching treatment to determine whether a greater diffusing effect could be obtained. These samples were first etched for 4 minutes in a solution containing 10 percent sodium hydroxide plus 8 percent sodium chloride, the solution being held at a temperature of 80 degrees Centigrade during the etching treatment. The samples were then removed, washed, dipped in the nitric acid solution, removed and washed. They were then etched again by immersing for two minutes in a hydrofluoric acid solution held at a temperature of 50 to 60 degrees Centigrade. After this treatment they were removed, washed, given a final nitric acid dip, and a final washing treatment.

In carrying out any of these etching treatments, the time of etching will depend somewhat on the results desired. Other conditions being equal, a more diffusely reflecting surface is produced by the longer etching periods; moreover, as the solution weakens by continued use, longer etching periods become necessary, or fortification of the solution with additional reagents is in order. The rate of etching is also slower at lower temperatures. When etching with either sodium hydroxide or hydrofluoric acid, the action is to preferentially dissolve aluminum and there may be left at the surface a dark colored film containing certain impurities such as iron, copper and silicon. The treatment with nitric acid is for the purpose of removing this film and leaving a bright clean surface.

In general, the best reflecting surfaces are produced on pure aluminum and sheet of commercial purity known as 2S. The aluminum-manganese alloy known as 3S may also be etched to give substantially as good results. Alloys with higher concentrations of alloying ingredients do not, in general, give as brightly reflecting surfaces as these materials.

TESTING OF SPECIMENS

Four types of tests were used in the measurement of the reflection characteristics of the specimens tested, as follows:

Diffuse reflection-factors for light were measured by use of a Taylor absolute reflectometer.[3] This instrument measures the light diffusely reflected when light from a small tungsten lamp is incident at an angle of 30 degrees from the normal to the surface.

Relative diffuse reflection-factors for ultraviolet radiation, weighted approximately in accordance with its effectiveness in producing sunburn or reddening of the skin, were determined by use of an eleven inch hollow sphere coated with magnesium oxide. The test specimen was placed over an opening in one side and light from the arc of a MAZDA Sunlight lamp (tungsten-mercury arc) was focused upon the test surface through a small hole in the opposite wall. At a point 90 degrees from the test surface, and screened from it, was placed a glass which fluoresced when exposed to ultraviolet radiation. Under the conditions of the test the spectral sensitivity of the device was as shown in Table 1. The fluorescent brightness of the glass was measured by use of a photoelectric cell and direct-current amplifier. Since the values obtained are relative *only*, they have been referred to a particular block of magnesium carbonate as the standard. The relative reflection-factors so obtained are shown in Table 2, together with the diffuse reflection-factors for light.

TABLE 1. *Spectral sensitivity of fluorescent photometer for measuring ultraviolet reflection-factors.*

λ	Relative sensitivity	λ	Relative sensitivity
2654A°	25	2967A°	92
2700	34	3024	68
2804	72	3132	33
2896	100	3342	3.3
2925	100	3663	0.04

Spectral reflection-factors in the ultraviolet were measured for several representative specimens. The method used was devised by one of the authors (AHT) and differs materially from any methods previously

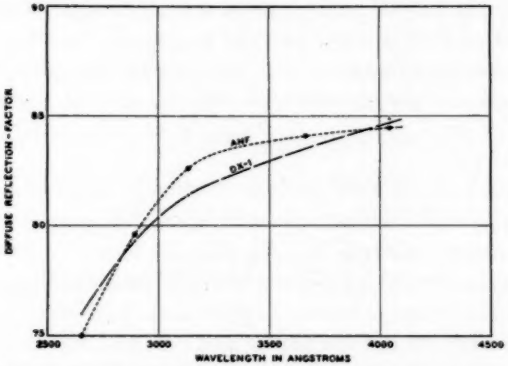

FIG. 1. *Spectral reflection curves for two specimens of oxidized aluminum.*

employed by other investigators.[4,5,6,7] The principles employed were the same as those in the Taylor[3] reflectometer for measurements of diffuse reflection-factors for light. In this apparatus, however, the light-source was a MAZDA Sunlight lamp in a quartz bulb outside the sphere, and an image of the arc was focused through a small hole in one side of the sphere onto the test surface placed over a larger hole in the opposite wall. A quartz monochromator (Hilger quartz spectrograph) was arranged to view a small spot at a point screened from the test specimen. The sphere could be rotated 90 degrees about an axis coinciding with the collimator axis of the monochromator, in which position the focused arc image fell upon a spot on the sphere wall not screened from the spot observed by the monochromator. The energy at any wave length was measured by a quartz sodium photoelectric cell and direct current

amplifier. (A complete description of the apparatus used in these tests will be published soon in the Review of Scientific Instruments). Spectral reflection curves for two specimens are shown in Fig. 1 and values at λ2967 for several specimens are given in Table 2.

For the measurement of light diffusion characteristics of the aluminum specimens, apparatus was devised in which a photoelectric cell measured the *relative* brightness of the specimen at various angles of view. The photoelectric cell was arranged to rotate about an axis in the plane of a flat specimen, and viewed a narrow strip of surface on each

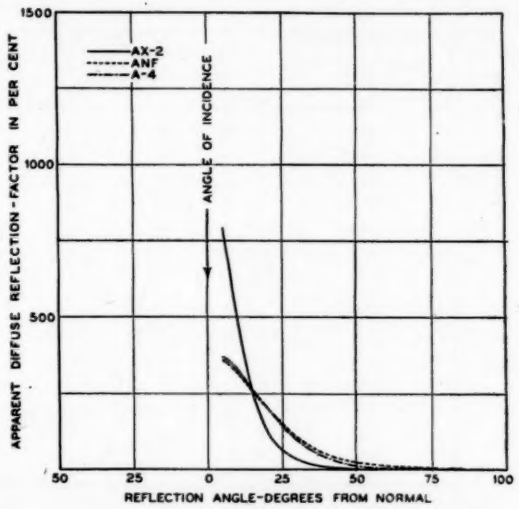

FIG. 2. *Diffusion characteristics of the light reflected from three specimens of oxidized aluminum when the incident light was perpendicular to the surface.*

side of the axis. The angles of incidence of the light and view of the surface could be independently varied. The brightness of the surface for various angles of reflection was measured when light was incident normally to the surface and at 45 degrees from the normal.

Fig. 2 shows the "apparent diffuse reflection-factor" at various angles from the normal, when three specimens were illuminated by light incident normally to the surface. These values are based on a value of 100 for a perfectly reflecting perfect diffuser, i.e., a surface which reflects all of the incident light and is equally bright at all angles of view. Fig. 3 shows the "apparent diffuse reflection-factors" for the same specimens when the light was incident at an angle of 45 degrees to the normal.

SUMMARY AND DISCUSSION OF RESULTS

Three methods of etching aluminum have been studied. All three produce partially diffusing surfaces having high reflection-factors for both light and ultraviolet radiation. Reflection-factors for light range between 82 and 87 percent, and for ultraviolet radiation at λ2967 the values for the etched specimens measured range between 81 and 82 percent. (These values for ultraviolet radiation are substantially higher than those found by Hulburt,[4] who measured aluminum films prepared by cathodic spluttering on glass.) This wave length was used because it

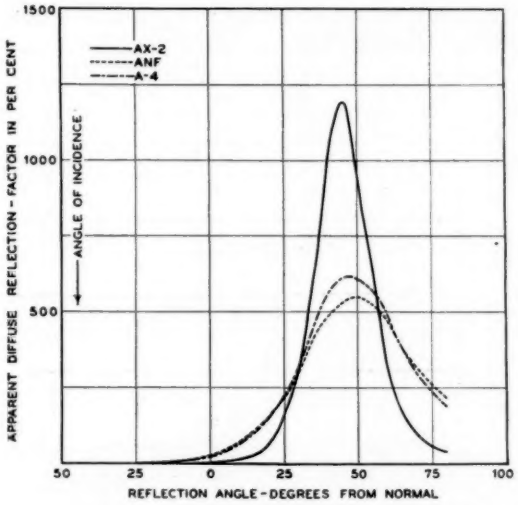

FIG. 3. *Diffusion characteristics of the light reflected from three specimens of oxidized aluminum when the light was incident at an angle of 45 degrees from the perpendicular.*

is at the center of a very narrow spectral band which is especially effective in producing erythema[8] (reddening of the skin), and also appears to be very potent in the cure of rickets.

It was found that etching the aluminum, even when the immersion was for a very short time, produced a large increase in reflection for light and a still greater increase for the ultraviolet (see Table 2). The same degree of increase was obtained when a piece of hard-rolled 3S aluminum alloy sheet was surfaced on the lathe by removal of the surface to a depth of approximately 1/32 inch. These tests would indicate that the sheet aluminum as it comes from the mill has a thin "skin"

which absorbs light and ultraviolet, and that etching in acid or alkali solutions removes it.

TABLE 2. *Diffuse reflection-factors for light, relative diffuse reflection-factors for ultraviolet (see text), and diffuse reflection-factors at λ2967 for various specimens of aluminum.*

Hydrofluoric acid etch—Specimens A-1 to A-8 and D-1 to D-8.
Sodium hydroxide-sodium fluoride etch—Specimens AX-1/2 to AX-2 and DX-1/2 to DX-2.
Sodium hydroxide-sodium chloride:hydrofluoric acid etch—Specimens ANF and DNF.
All samples marked A and D were from two different lots of aluminum sheet (2S), and the number after the letters indicates the number of minutes the specimen was immersed in the etching reagent, hydrofluoric acid, for example.

Specimen	Diffuse reflection-factor for light	Relative diffuse reflection-factor for ultraviolet	Diffuse reflection-factor at λ2967
A-1	85 per cent	118	—
A-2	86	118	—
A-3	87	—	—
A-4	84	124	82
A-5	87	123	—
A-8	85	119	—
D-1	84	116	—
D-2	82	118	—
D-3	86	116	—
D-4	86	116	—
D-5	85	118	—
D-8	84	119	82
AX-1/2	84	121	—
AX-1	84	121	82
AX-2	84	118	—
DX-1/2	82	114	—
DX-1	83	115	81
DX-2	84	115	—
ANF	83	—	81
DNF	84	—	—
Mill finished A	64	—	39
Mill finished D	70	—	—
3S sheet aluminum	53	—	33
Same, surfaced on lathe	82	—	78
Aluminum, 99.9 per-cent pure	87	—	—
Magnesium carbonate	. 98	100	73

All of the specimens tested showed an appreciable specular characteristic in their reflection, as will be seen by reference to Figs. 2 and 3. Apparently the gloss or mattness of the surface of the sheet metal before etching has some effect upon the diffusion characteristics after etching.

The A material (Table 2) was more glossy than the D material before etching, and all of the etched specimens showed that the effect of this glossiness was retained to some extent after etching.

While all three etching methods used gave good results, we believe that the use of hydrofluoric acid is less desirable from the standpoint of convenience in handling the reagent. It should be held in hard rubber containers and contact with the skin avoided. The sodium hydroxide-sodium fluoride method gives good results in a short time of etching, and appears to be preferable to the other two methods.

Aluminum etched by other solutions has been studied in the laboratory, and reflection-factors slightly below those shown in Table 2 have been observed for a number of specimens. Since there are many solutions which can be used it is quite possible that some of them might give results equal to the methods described here, but it is improbable that the reflection-factors which we have obtained would be appreciably exceeded.

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CHARACTERISTICS OF THE GENERAL ELECTRIC PHOTOFLASH LAMP

By W. E. Forsythe and M. A. Easley

[Lamp Development Laboratory, General Electric Company, Nela Park, Cleveland, Ohio. Received July 24, 1931]

The new photoflash lamp, as the name implies, is a lamp intended for taking flashlight pictures. This requires an intense flash of light which is produced in this lamp by the burning of very thin aluminum foil in the presence of a slight excess of oxygen. Fig. 1 shows a picture of the lamp.

Fig. 1. *Picture of photoflash lamp.*

The bulb of the flash lamp contains about 170 mm of pure oxygen and about 65 mg of aluminum foil that is about .00004 cm thick and has an area of about 600 square centimeters. To start the foil burning the filament of the lamp is covered with a paste that ignites when the filament is heated by the electric current. The lamps are now constructed so that they may be flashed on any voltage from that of about two dry cells up to that of the 120 volt lighting circuit.

As shown in Table 1 the time of starting the flash after closing the electric circuit depends upon the voltage used. However, after the lamp

starts, the starting voltage has no influence on the rate or duration of the flash.

Since this lamp flashes so quickly the methods used in studying the characteristics of other lamps could not be applied here. It was found that the total quantity of light radiated by the lamp could be measured by the ballistic throw of a sensitive galvanometer connected to a photoelectric tube. This photoelectric tube-galvanometer combination was calibrated for quantity of light by exposing the tube to a high intensity tungsten lamp for a short time (.15 seconds), by means of a pendulum device and reading the resulting throw of the galvanometer. To make the results of the photoelectric tube record as nearly as possible the lumen output of the lamp a special piece of green glass was mounted in front of the tube. By calculation it was found that this green glass-

TABLE 1. *Some characteristics of the average photoflash lamp.*

Light output in lumen seconds	47,000
Maximum intensity in lumens	4,500,000
Time from closing electric circuit to starting of flash	
Flashed with 3 volts	.025 sec
Flashed with 6 volts	.024 "
Flashed with 110 volts	.009 "
Time from start of flash to maximum of flash	.014 "
Duration of flash	.066 "

photoelectric tube combination gave within about 10% of what would have been obtained by the average eye. This error was corrected for in the final results.

A special test using both the high intensity tungsten lamps and a number of flash lamps showed that the intensity-deflection relation of the photoelectric tube-galvanometer combination as used ballistically was linear over the range that was used in calibrating the equipment and in measuring the photoflash lamps.

To measure the time relations of the flash lamp a falling plate flashometer[1] was used. By the use of the flashometer the time from the closing of the electric circuit to the start of the flash, the time to the maximum of the flash, and the total duration of the flash could be determined to a little better than one thousandth of a second. The time scale of the flashometer was obtained by the known method of focusing on to the falling plate across the slit the image of a carbon filament heated by alternating current. By bringing a magnet near the filament it could be

[1] Rev. Sci. Inst. *2*, 638-43, 1931.

caused to vibrate with a period equal to that of the alternating current. The time of exposure of the photoelectric tube by the pendulum device was also determined by this vibrating carbon filament. The relative time-intensity relation of the lamp was obtained from measurements of the density of the photographic trace on the falling plate for plates that had been calibrated for the relation between light intensity and photographic density. This calibration was obtained both from tungsten lamp sources at different distances and by the use of a number of photoflash lamps at different distances. Some of the characteristics of the average photoflash lamp are given in Table 1.

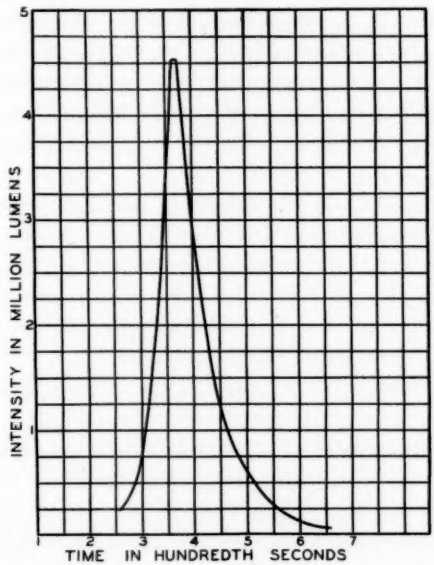

FIG. 2. *Time-intensity relation for the average photoflash lamp.*

The curve in Fig. 2 shows the average time-intensity relation of certain flash lamps in lumen seconds. This curve was reduced to lumen seconds by making the area under the relative time-intensity curve obtained by the use of the falling plate flashometer equal to the total quantity of light given by the average photoflash lamp.

Dr. E. Q. Adams of our Laboratory made some calculations of the temperature that might be reached by the aluminum oxide when one of these lamps was flashed. The amount of energy produced by burning

the 65 mg of aluminum in an excess of oxygen was calculated to be about 1500 watt seconds. Since this flash occurs in so short a time it was assumed that this energy would not have time to be radiated, but for the most part would be used to heat the aluminum oxide. Knowing the specific heat of aluminum oxide and also something about the change of specific heats of solids and liquids with a change of temperature he was able to obtain an approximate upper limit to the temperature. The value for the upper limit that he obtained was 9500°K.

If one of these lamps is flashed within about a centimeter of another lamp the second lamp will also flash. It was found that foil such as that used in the lamp could be ignited if held in the open near a lamp that was flashed. If the foil were much thicker than that used in the lamp it could not be ignited by the flashing of the lamp either with the foil in a lamp or out in the open. It was found possible to ignite both the foil and the lamps by focusing sunlight upon them. However, neither the lamps nor the foil could be flashed by holding them as near as possible to a 10 kilowatt tungsten lamp.

Some photoflash lamps were made up that did not contain oxygen. When these lamps were held near other lamps as they flashed evidence was found that the aluminum had been heated hot enough to melt it. Of course it did not burn. All these experiments seemed to prove that the radiation from the flash lamp falling upon the thin aluminum foil raised it to a temperature sufficient to ignite it.[2]

The average maximum intensity of the light output of the lamps tested was found to be about 4,500,000 lumens. If this 4,500,000 lumens be reduced to mean spherical candlepower by dividing by 4π the result is 360,000. The projected area of the bulb is about 40 square centimeters, which gives an average brightness of about 9,000 candles per square centimeter. Some years ago Dr. Ives[3] measured the emissivity of aluminum oxide for visible radiation and obtained a figure of about 9% for a temperature of about 1800°K. Thus if the emissivity of the aluminum oxide does not change with an increase in temperature a black body at the temperature of the oxide in the lamp would have a brightness about eleven times that obtained for the lamp or about 100,000 candles per square centimeter. This brightness of a black body corresponds to a temperature of about 5000°K. Another consideration to be remembered is that there is probably not enough

[2] Naturwissenschaften, *41*, 867, Oct. 1930.
[3] J. Franklin Institute, *186*, 437; Oct., 1918.

aluminum oxide in the bulb to make a continuous solid radiator even when only the projected area is considered. It probably radiates somewhat like the Welsbach mantle, that is, there are a number of dark spaces with some radiating material surrounding them. The temperature is therefore probably higher than the calculated minimum value and lower than the maximum. All the data indicate that the temperature reached in the lamp is probably between 5000° and 9500°K.

A spectrogram of the radiation from a photoflash lamp shows a few bright lines, a number of bands, and a continuous background. The ultraviolet radiation extended to about 3000A but was not very intense as shown by the spectrum and there were no lines in this part of the spectrum strong enough to show through the continuous background. Between twenty and thirty bands and lines have been measured and identified as belonging to aluminum oxide and to aluminum. Some bands obtained in the spectrum have not been identified, but they are probably radiated by constituents of the paste that is put on the filament.

Some comparisons between the photoflash lamp and incandescent lamps are interesting. In Table 1 the total quantity of light is given as about 47,000 lumen seconds. This means that one would have to look at a 100 watt Mazda lamp for about 37 seconds to get the same quantity of light as from the flash lamp, or that the same quantity of light would fall upon the eye if exposed to a 500 watt Mazda lamp for about 5 seconds. It would require 470 five hundred watt incandescent lamps to give the same maximum output as that given by one photoflash lamp. A 10 kilowatt lamp, manufactured for special purposes, radiates in such a manner as to have an efficiency of about 27 lumens per watt. A 50 kilowatt lamp has been made after the same design as the 10 kilowatt lamp. The intensity of the light in the direction perpendicular to the plane of its filament is about 166,000 candles. It is thus seen that the intensity of the light from the photoflash lamp at its maximum is about twice as great as the maximum of the 50 kilowatt lamp. The total amount of energy produced in this lamp by burning the aluminum is about 1500 watt seconds. Combining this with the total light output of the lamp of 47,000 lumen seconds gives an efficiency of about 32 lumens per watt.

THE CONSTRUCTION AND OPERATION OF CAPILLARY MERCURY ARCS*

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[Columbia University, New York, New York.
Received June 1, 1931]

Two branches of investigation have required a source of radiation of high intensity. In the study of photochemical reactions with low quantum yields by means of a monochromator the restriction of the available area of the source by the slit requires either a large condensing lens or a source with very much greater intensity than is available with an ordinary commercial arc. Also, studies of weak scattered radiation, can be carried out with more convenient exposure times if the primary source is of a much higher intensity than ordinarily available. These considerations have given rise to the development of the capillary mercury arc whose intensity per unit area can be made many times that of commercial arcs.[1] The high energy input causes, however, a rapid deterioration in the structure of the quartz and the development of a brownish deposit. These consequences result in such a rapid decrease in the emission of the lamps[2] that their usefulness is seriously compromised. (See Curves I, II, III of Fig. 3.)

The construction and operation of the lamp to be described are such that it can be burned with a high energy input and yet prevent both the rapid decrease of intensity and the deterioration of the quartz.

The Nature of the Problem and Experimental Development

The loss in emission of these arcs is due to the gradual deposition of absorbing materials. The character, location and rate of formation of these substances depend primarily on the temperature which in turn is determined by the energy dissipation in the various parts of the arc and the manner of the cooling process. For instance, at moderate temperatures brown material and at high temperatures whitish material appears, at low temperatures the formation is slow and usually occurs in the region of the anode where the temperature is higher; if the input is increased the higher anode temperature now causes a shifting of the material in the direction of the cathode, higher inputs result in a white

* Contribution No. 662, from the Department of Chemistry.
[1] Harrison and Forbes, J.O.S.A. *10*, 1; 1925.
Forbes and Harrison, J.O.S.A. *11*, 99; 1925.
[2] Forbes and Harrison, J.A.C.S., *47*, 2449; 1925.
Lange and Meggers, Bur. Stds. J. Res. (5), *4*, 711; 1930.

instead of the black deposit. These changes would occur for example in a capillary of 2 mm bore and a 3–4 mm wall approximately as follows: brown deposit forms if burning under water at 4–6 amperes, this shifts at 6–10 amperes; if then burned in air around 6 amperes the brown deposit disappears and a white deposit forms slowly, at 8 amperes this shifts to the colder parts and at 10 amperes the vaporization of the quartz is quite apparent. A greenish fluorescent glow was frequently observed under these extreme conditions. At these higher temperatures the quartz crystallizes rapidly. It has been found for example that the complete devitrification of a sample of powdered quartzglass required 35 days at 1063 C, 6 days at 1160, 3 days at 1200, 2 hours at 1500, and 1 hour at 1600.[3]

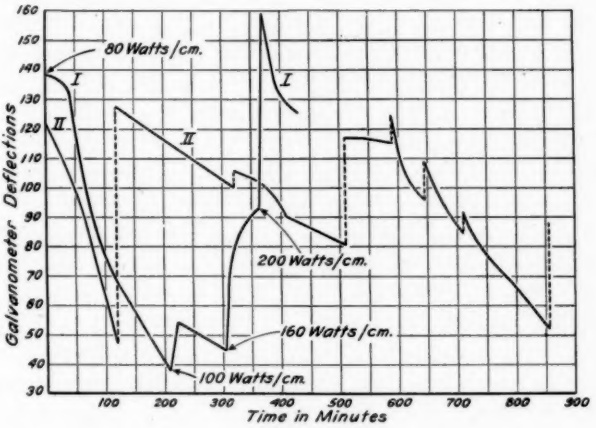

FIG. 1

Curve I. Capillary 5 cm long, 0.7 mm wall, 2 mm bore. Burned under water. Wattages applied at points indicated by arrows. Observations made on blue line.

Curve II. Lamp burned under water. Renewed at breaks by burning front in air and cooling rear with running water. Differences of renewals due to various inputs during the operation. Cleaning of front by this process does not change rate of decay on further operation. Observations made on λ365.

With these facts in mind it was planned to build an arc that could be operated at temperatures between the formation of the two deposits. If the capillary wall were quite thin the temperature at a low input should be well below the formation of black material and it should be possible to increase the input until a satisfactory temperature would be obtained.

[3] Sosman, *The Properties of Silica* p. 99, American Chemical Society Monograph, 1927.

The lamp constructed had a capillary of 2 mm bore and 0.7 mm wall and was 5 cms long. It was somewhat difficult to immerse the lamp in time to prevent melting of the thin wall. The intensity of the blue line was followed with a thermopile and the results are shown in Curve I, Fig. 1. It is apparent from the rapid drop after each increase that no input between 500 and 1000 watts filled the conditions satisfactorily. An attempt was then made to keep a constant moderate input and change the cooling till a proper temperature would be achieved. This was accomplished by blowing a stream of air with various amounts of atomized water over the capillary. The result was no better. Likewise efforts to move the arc to one side with a magnet or by bending the capillary in order to get temperature differences proved of no use. An effort was also made to remove the black material from the front during the operation of the lamp by periodically burning it with the front in air and the rear cooled with water. The input was also temporarily increased. The results are given in Curve II of Fig. 1. It can be seen that this procedure is fairly efficient in clearing the front but deterioration after each "renewal" proceeds as before.

It seemed unlikely that the tube as a whole could be controlled at a satisfactory temperature so that the next step was to control the temperature in the various parts of the capillary and thereby determine the location of the deposit. The lamp was the same as used previously.[4] See also Fig. 2. The capillary, 2 mm bore, 3 mm wall, 50 mm in length, was ground flat on the side away from the slit until the wall thickness was reduced to about 0.5 mm. The slit side was ground until a face of about 3 mm width was obtained, thus reducing the apparent size of the capillary. A very satisfactory polish was obtained on both sides by first cleaning the ground surfaces with hydrofluoric acid and then carefully heating with a sharp flame. The lower electrode was sealed in with De Khotsky cement and the exposed end covered with a thin coat of the cement to prevent rusting. The ends of the electrodes immersed in mercury were oxidized in a hot flame which prevented any wetting. The quartz at the upper electrode was constricted sharply as indicated and the electrode was slightly tapered to insure a close fit. If the fit is too close it must be notched lengthwise to permit the flow of mercury incident to striking the arc. In case the whole length of the capillary is heated on starting as when it is partially enclosed by copper gauze the electrode must be lifted somewhat to take care of the sudden pressure

[4] Crist, R.H., J.A.C.S. *52*, 4337; 1930.

increase when the arc strikes. Filling the capillary with several wires has been found unsatisfactory as the mercury does not wet the iron and will not enclose the wires thus permitting access of air to the electrode when the lamp is turned out. It was found also that the intensity is much more constant if the upper mercury surface oscillates very slightly instead of being rigid. This phenomenon can be understood from the characteristics of mercury arcs.[5]

The De Khotinsky seal and the back part of the lamp were cooled with running water[6] as described previously.[7] The lamp was operated on about 90 volts and 4.5 amperes. The quartz began to devitrify after some twenty hours burning under these conditions. The capillary was then replaced and the front was cooled by a stream of air but the control was too uncertain and the air stream had to be made intermittent by a long lag relay circuit. This was arranged by putting a small flame under the coil of a small mercury regulator and adjusting these at the intake of the sirrocco so that the flame was drawn away from the coil after contact was made in starting it. In this manner a fairly constant intensity can be maintained. However, a white deposit forms slowly and this can be removed only if the input is increased dangerously high. This operation constitutes a vaporization of silica which then deposits on the cooled part of the capillary.

If the bore of the capillary is larger less difficulty is experienced with the evaporation of silica. A lamp was constructed with the dimensions 3 mm bore, 7 mm o.d., 50 mm long, the rear wall being ground to about 0.5 mm. This lamp was operated on 65 volts and 6.5 amperes. The brown material deposited heaviest along the sides of the capillary and after a time in the front. On long burning, whitish material appeared first at the anode end and gradually on the front. The brownish deposit was removed by increasing the input and also by heating the capillary with the oxy-gas flame. There was also the unexpected result that no deposit appeared on the back which was the coldest part of the tube. Some typical results of the decrease of the intensity with the time are shown in Curves I and III of Fig. 3.

The last form of the lamp was as given in Fig. 2. The dimensions were 3 mm bore, 7 mm o.d., 50 mm long. Because of the previous ob-

[5] Buttloph, L. J., *The Electrical Characteristics of Commercial Mercury Arcs.* Rev. Sci. Inst. *1* (9) 487, 1930.

[6] If a large electrode and high melting De Khotinsky were used cooling would not be necessary.

[7] Crist, R. H., J.A.C.S., *52*, 4337; 1930.

servations that the brown material did not deposit in the cold part of the tube the wall was left the same thickness throughout. The cooling was accomplished by running water over wire gauze fitted to the lamp. A piece of gauze is cut as in Fig. 2*A* and is then put around the capillary with the edges shaped back as in Fig. 2*B* the edge being pressed

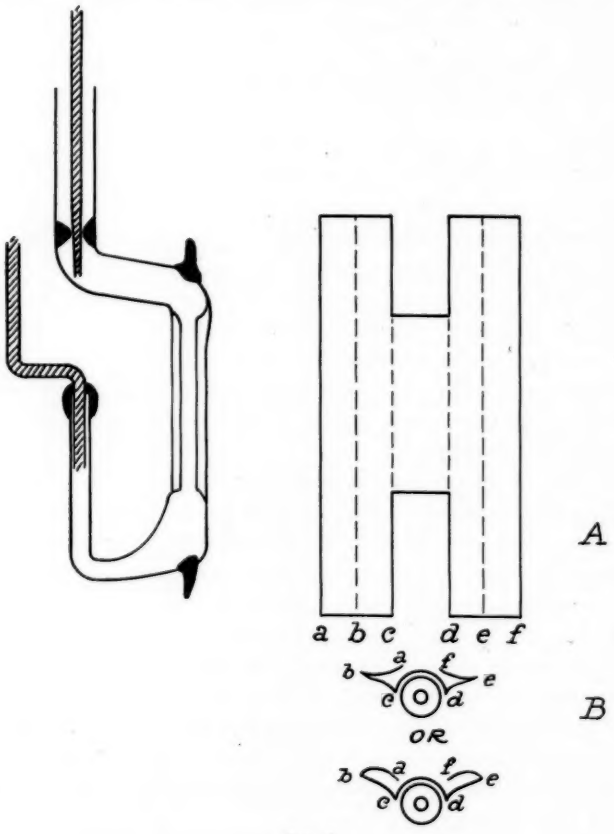

FIG. 2

very thin. It is best to make the edge with a pair of pliers then open the gauze and shape it as indicated in the figure. The extended parts of the gauze in *A* are carried around above and below the electrode parts and twisted together. Water will then flow down the gauze and by cohesion will be pulled from the edges into the flanged part in *B*. In case the

water creeps around the edge and deposits carbonates in the line of vision they can be removed with concentrated hydrochloric acid.

The lamp described above was operated on 90 volts and 5.5 amperes and the gauze covered 1/3 of the tube. The black deposit formed in a short time (twenty minutes) on the back but none appeared on the front after burning thirty hours.* The thermopyle readings were taken for λ 265 and the results are shown in Curve IV of Fig. 3. The fall and rise at sixteen hours was probably due to the change in cooling that favored the black deposition which was removed when the cooling was not so rapid. The increases at seventeen and one-half and twenty-two and one-

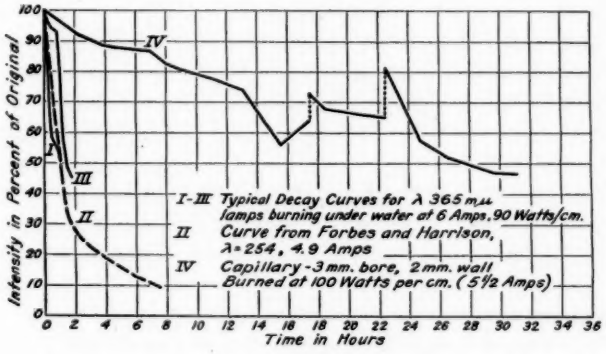
Intensity in Percent of Original
Time in Hours
I-III Typical Decay Curves for λ 365 mμ lamps burning under water at 6 Amps, 90 Watts/cm.
II Curve from Forbes and Harrison, λ=254, 4.9 Amps
IV Capillary - 3 mm. bore, 2 mm. wall Burned at 100 Watts per cm. (5½ Amps)

FIG. 3

half hours are a result of heating to relight the lamp. At thirty hours signs of devitrification began to appear on the front and the lamp was removed, cleaned and the capillary softened in the flame. It was then operated with the one side instead of the front facing the slit. In this way the two sides and the front can in turn be used to get some seventy-five hours satisfactory use before the capillary must be replaced. There is indeed difficulty in complete fusion of the capillary as the crystallized layer on the inside fuses at a higher temperature than the vitreous outside so that it has been found more satisfactory not to attempt complete revitrification but to use another part of the tube.

* The rate of the cooling water must not be too great as the temperature of the various parts of the capillary may then be such that the front is just right for the formation of the black deposit. It works best when the water on the back of the capillary sputters through the gauze a little.

THE NATURE OF THE DEPOSIT

Thus far the chemical nature of the brown deposit has not been considered. Various views have been presented. Tolansky[8] thinks that the coloration is due to mercury atoms becoming imbedded in the walls and from which they can be readily expelled by heating. It seems difficult to understand why this should not occur with a cold wall but should require a definite higher temperature. Also it was found on boiling out the mercury in the lamp preliminary to operation that if the mercury were expelled from the capillary and the quartz heated to redness a deposit appeared. Its formation and removal with heating were quite similar to that of the deposit formed during the operation of the lamp.

If the black material is decomposed by heating or by increasing the input small bubbles collect in the mercury at the upper electrode. The walls are a permanent source of gas as is shown by the fact that heating to redness for a considerable time did not prevent further emission of gas nor decrease the rate of formation of deposit. The facts presented can be correlated with the properties of the oxygen and nitrogen compounds of mercury. Mercuric oxide begins to form at about 360° and decomposes at 500°. This would explain the non-formation on the hot and cold parts and the formation at the intermediate temperatures. The formation of silicon or of silicon monoxide from the bombardment by electrons or metastable mercury atoms is also a possibility. The heat of formation of silicon dioxide from Si and O_2 is 161,000 calories and the energy available in metastable mercury atoms is considerably less, namely, 107,000 calories. However, the process could go in two stages with SiO as an intermediate. The formation of such materials is indicated by the fact that there was a residue which dissolved in hot alkali.

THE CHARACTER OF THE EMISSION

This part of the investigation was concerned with the character of the various lines. Photographs were taken on a 21 foot grating. The lamp was burning under water at 9 amperes and 20 volts per cm. In addition to reversals observed in hot high pressure mercury vapor lamps there was strong reversal in the sharp lines λ 4047. ($2^3P_0-2^3S_1$) and λ 4358 ($2^3P_1-2^3S_1$). There was no absorption of λ 3341 ($2^3P_2-3^3S_1$). Photographs were also taken when the lamp was burning under 60 mm and also under 20 mm pressure. Under these conditions absorption per-

[8] Proc. Phy. Soc. *42* (5) 556; 1930.

sists in λ 4358 while in λ 4047 it is just detectable. The width of λ 4047 was found to be 0.3 A. These considerations are of primary importance in the application of the lamp to the problems of light scattering as in the Raman effect. The separations found for the rotation shifts of the hydrogen halide gases and for vibrational shifts in gases and liquids are sufficiently large for the use of λ 4047 to yield satisfactory results. The rotational separations of molecules with heavy nuclei are of the order of magnitude of the width of the exciting line so that this source would not be useful in such investigations.

The author desires to thank the Department of Physics of the University for the use of the grating.

Spectroscopy—Emission and Absorption Spectra, Electro- and Magneto-optics (Numerical Data). M. L. Bruninghaus, V. Henri, and F. Wolfers. Extracted from Volume VII of Annual Tables of Constants and Numerical Data (Years 1925-1926); I vol. 4–to, Pp. xviii+514. Price—Cloth: Frs. 190; Paper: Frs 170. Gauthier-Villars et Cie. Paris, Sold through McGraw-Hill Book Co., New York.

The Book, as the title indicates, is a book of data gathered from periodicals in the years mentioned. Where possible a brief abstract of the paper is given together with the numerical data. In the case of absorption spectra a great many curves are shown. The publishers have done their part well and the tables are easy to read. The text appears in French and in English.

J. R. COLLINS

Traite de Pyrometrie Optique. By Gustave Ribaud, 485 pages. This book is part IV of the fifth section of an Encyclopedia on photometry published by Revue d'Optique Theoretique et Instrumentale, at Paris.

Professor Ribaud has collected in this book an enormous amount of information on pyrometry and related subjects. The various laws of radiation of both black bodies and non black bodies are given and discussed and what is more interesting is the amount of reference data and different methods of handling and presenting data which are included. In presenting the radiation laws an error that is quite general is followed. On page 48 it is stated that the equation, $\lambda_m T = \text{constant}$, is the common mathematical expression for Wien's displacement law. Professor Ribaud gives the displacement law in the proper form in paragraph 31 but presents this principal corollary as the general mathematical expression rather than the more general form.

Different methods of measuring temperature and the related physical phenomena are given together with descriptions of both the source being investigated and the different instruments used. The various sources of errors that are encountered and methods for avoiding them are outlined. Not only are the theoretical relations given but the general practical methods for making the measurements are included. The standard methods of establishing and maintaining the temperature scale for the entire range of an optical pyrometer including a description of the black body sources, special sources and optical pyrometer are well outlined. Various methods are given for calibrating the optical pyrometer and for extending its calibration to the highest temperature desired. In keeping with what seems to be the best practice, the author outlines his reasons for preferring the disappearing filament type of optical pyrometer. There are also included methods of measuring the brightness, true and color temperature of non black body sources. One very commendable feature is the very extended author and title index that is given. This book should be a very valuable addition to the literature on this subject.

W. E. FORSYTHE